# Compounds of Organotin (IV) Halides with Sulphur and Nitrogen Donor Ligands

# ABSTRACT

A THESIS SUBMITTED TO
THE ALIGARH MUSLIM UNIVERSITY, ALIGARH
FOR THE DEGREE OF

**DOCTOR OF PHILOSOPHY**
**IN**
**CHEMISTRY**



Department of Chemistry
Aligarh Muslim University,
Aligarh, India.

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September, 1982

## ABSTRACT

A study of the addition as well as substitution compounds of some organotin(IV) halides or acetates, viz., triphenyltin chloride or acetate, tributyltin chloride, dibutyltin diacetate and trimethyltin chloride with a few biologically active ligands containing nitrogen or sulphur or both namely, piperazine (bis) dithiocarbamate(Pz (bis) dtc), diethyldithiocarbamate($Et_2$dtc), acridine (acr.), piperazine (Pz), pyrrolidine (pyrr.), 1,10-phenanthroline (Phen.), 2,2'-bipyridyl (bipy), pyrazolones namely, antipyrine and 4-amino antipyrine, benzo(c)-, benzo(f)- and benzo(h)-quinolines and 5,6-dimethyl-benzimidazole, 2,5-dimercapto-1,3,4-thiadiazole (Bismuthiol I), and 2-benzimidazole thiol has been made. The composition of the solid complexes has been established on the basis of elemental analysis. Infrared spectral studies (4000-200 $cm^{-1}$) have been made to elucidate the structure and stereochemistry of the complexes. Changes in the I.R. frequencies of different groups upon coordination have been studied and the coordination sites proposed. The far infrared spectra of the complexes in the region 650-200 $cm^{-1}$ have been recorded to assign the metal-halogen and metal-ligand stretching vibrations and to establish, therefrom, their stereochemistry. The molar conductances of the soluble complexes have been measured and indicated that they were basically non-ionic in nature. Substitution compounds of

trialkyltin(IV) halides with piperazine bis dithiocarbamate Pz(bis)dtc and diethyl dithiocarbamate, $Et_2$dtc, have been synthesised to examine whether it acts as a unidentate, bidentate or quadridentate ligand and to establish the structures of these complexes. The I.R. studies revealed that piperazine bis dithiocarbamate can act both as a bidentate or a quadridentate ligand coordinating through one or both dithiocarbamato units in the present case. The diethyl dithiocarbamate showed a bidentate behaviour in all the complexes. A pentacoordinated tin atom with a trigonal bipyramidal geometry has been proposed for these organotin(IV) dithiocarbamates. Molecular complexes of organotin (IV) halides with some nitrogen bases namely, acridine, piperazine, pyrrolidine, 1,10-phenanthroline and 2,2'-bipyridyl have been characterised and site of coordination has been explored. Trialkyltin (IV) halides form two types of complexes with monodentate ligands, $R_3SnX.L$ and $R_3SnX.L_2$, where L is the ligand. It is found that in all the cases the tin atom is metallated through ring nitrogen which is the only possible site for coordination. These adducts have been found to have a 1:1 metal to ligand ratio and exhibit non-ionic character in nitrobenzene or methanol. A trigonal bipyramidal geometry has been suggested for acridine, piperazine and pyrrolidine complexes while for phenanthroline and 2,2'-bipyridyl complexes a cis octahedral geometry has been suggested.

The pyrazolone complexes of the type $R_3SnX.L$ and $R_2SnX_2.L$ where R = phenyl, butyl or methyl and X = chloride or acetate

have been synthesized to study the coordination behaviour of pyrazolones and to establish the structure of the complexes. All the complexes are found to have a 1:1, M:L ratio. The I.R. spectra indicate coordination through carbonyl oxygen in all the complexes. In 4-amino antipyrine complexes the amino group is also found to be coordination active. These complexes showed too low values of molar conductance confirming their non-ionic behaviour.

Addition compounds of benzo(c), - benzo(f)- and benzo(h) quinolines of the general formula $R_3SnX.L$, $R_2SnX_2.L$ and $R_3SnX.L_2$ have been synthesized to study the nature of bonding of the metal to the ligand. In benzo quinolines the only coordination site is the ring nitrogen atom. The tin atom in quinoline complexes of $R_3SnX$ and $R_2SnX_2$ is found to be pentacoordinated while in triphenyltin chloride and tributyltin chloride complexes of benzo(c) quinoline tin atom is found to be hexacoordinated. A trigonal bipyramidal geometry has therefore, been proposed for five coordinate tin atom and an octahedral geometry has been proposed for hexacoordinated tin atom.

Benzo(h) quinoline has a peculiarity in the sense that it can form simultaneously metal-nitrogen and metal-carbon sigma bond by abstraction of a proton from carbon atom at position ten. In the present study, an attempt has been made to exploit this unusual behaviour of benzo(h) quinoline. It was found that with organotin(IV) halides benzo(h) quinoline forms only a metal-nitrogen bond and no M-C bond. However, when Bhq was allowed

to react with tin tetrachloride, the formation of metal-nitrogen and metal-carbon sigma bond was observed. It seems reasonable in view of fact that unlike organotin(IV) halides the tin tetrachloride does not have the bulky organic groups attached to the metal which prohibits the close approach of the tin and the ligand orbitals necessary for M-C $\sigma$ bone formation.

Donor-acceptor complexes of organotin(IV) halides of the type $R_3SnX.L$ and $R_2SnX_2.L$ where R = phenyl, butyl or methyl and L = 2,5-dimercapto-1,3,4-thiadiazole (Bismuthiol I), 5,6-dimethyl-benzimidazole and 2-benzimidazole thiol have been synthesised and characterized. On the basis of I.R. spectral studies, it has been suggested that coordination of metal occurs through the exocyclic sulphur atom in Bismuthiol I complexes.

A lowering of $\nu$(CN) in the complexes of 5,6-dimethyl benzimidazole suggests the coordination of the tin atom through tertiary nitrogen atom of the imidazole ring. The I.R. spectral study of the trimethyltin chloride adduct of benzimidazole-2-thiol, TMT (BIT), supports coordination of the benzimidazole-2-thiol moiety via its pyridyl nitrogen to the tin atom.

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Certified that the work embodied in this thesis entitled "Compounds of Organotin (IV) halides with Sulphur and Nitrogen donor ligands" is the result of original researches carried out under my supervision by (Miss) Fatima Razia Zaidi and is suitable for submission for the award of the Ph.D. degree of Aligarh Muslim University, Aligarh.

(K.S. SIDDIQI)

## ACKNOWLEDGEMENT

I take this opportunity for expressing my sincerest thanks to Dr. K.S. Siddiqi who has guided me with zeal and enthusiasm throughout the period of investigations. I am also very grateful to my respected teacher Professor S.A.A. Zaidi, A.R.I.C. (London) who inspired me and provided the necessary incentives.

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Thanks are due to all my research colleagues for the help they have rendered me from time to time.

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Fatima Razia Zaidi

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CONTENTS

## PUBLICATIONS

1 Piperazone bis (dithiocarbamate) and diethyl dithiocarbamate complexes of some triorganotin compounds.

K.S. Siddiqi, F.R. Zaidi and S.A.A. Zaidi.
Synth. React. Inorg. Met.-Org. Chem., 19(6), 969-978 (1980).

2 Complexes of triorganotin (IV) halides with some nitrogen containing ligands.

K.S. Siddiqi, F.R. Zaidi, N.S. Neelam and S.A.A.Zaidi.
Synth. React. Inorg. Met.-Org. Chem., 12(1), 71-82 (1982).

3 The ligand properties of quinolines, complex formation and metallation with group (IV) metal halides and organotin (IV) halides.

K.S. Siddiqi, F.R.Zaidi, T.A. Khan and S.A.A. Zaidi.
Bull. Soc. Chim. France (Communicated).

## LIST OF TABLES

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A lowering of $\nu$ (CN) in the complexes of 5,6-dimethyl benzimidazole suggests the coordination of the tin atom through tertiary nitrogen atom of the imidazole ring. The I.R. spectral study of the trimethyltin chloride adduct of benzimidazole-2-thiol T$^{n}$T (BIT) supports coordination of the benzimidazole-2-thiol moiety via its pyridyl nitrogen to the tin atom.

# CHAPTER I

## INTRODUCTION

# INTRODUCTION

Recent researches in organometallic chemistry have gone up exponentially due to their impact and importance in different disciplines. Organometallic compounds of group(IV) elements have shown great biological activity in general and organotin compounds in particular.[1]

Group(IV) elements beyond the second period have low energy d orbitals. They expand their valence shell by using these orbitals for coordination with Lewis bases. There is an increase in the metallic character with increasing atomic number in the group(IV) elements. There are three possible ways in which an element of group(IV) could form compounds:

(a) by loss of all four valence electrons to form the $M^{4+}$ ion.

(b) by hybridisation of the available atomic orbitals in a suitable manner to form four $\sigma$- or $\pi$ bonds.

(c) by expanding the octet and making use of the empty d orbitals in a $d^2sp^3$ hybridisation to form adducts with Lewis bases.

In the case of Sn(IV) compounds one could predict a spherical ion of radius 0.74 Å for ionic bonding and an octahedral hexa-coordination in most of the complex compounds.

The recent work on group(IV) metal chemistry is concerned with the synthesis and characterisation of their organometallic

compounds with a view to studying their biocidal activity.[1-6] Both dialkyl and trialkyltin compounds are being used on an increasing scale for a number of biocidal purposes. These compounds have significant use as heat stabilizers for polyvinyl plastics, as catalyst in plastic industry, as biocides for antifouling paints, as timber preservatives, as moth proofing agents, as crop protectants and in certain skin and blood diseases.

Triphenyltin acetate and hydroxide are well established agricultural fungicides especially for the control of phytophthora infestants on potatoes and cercospora on sugar beet. These compounds also exhibit insecticidal activity, mainly through their antifeedant function, i.e., rendering leaves of crops unpalatable to the insect pest, which therefore starves to death. Triphenyltin compounds have found satisfactory use for treating fungal diseases in cocoa, coffee, onions, bananas and pecan nuts. Complexes of triphenyltin compounds with dimethyl sulphoxide and quinoline-N-oxide have been reported to be effective for protecting tomatoes, celery and sugar beet and to be low in mammalian toxicity.

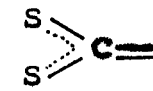
Rubber pellets containing tributyltin oxide are used for eradicating the snail carriers of Bilharzia. Triorganotin compounds are found to be effective against mosquitoes also. Organotin compounds are also used as an oxidant in rubber industry, and in making electrically conducting film over the surface of glass, as lubricating oils and as ingredient in certain veterinary medicines.

Extensive work has been done on various aryl and alkyl dithiocarbamates and their complexes with metal ions.[7-9] The alkyl, haloalkyl,[10,11] cycloalkyl, alkylene, phenyl, benzyl, pyridyl, tolyl,[12] pyrrolidine,[11] aniline, tetra hydroquinoline,[13] sulphonyl imido benzoyl, furfuran,[14] triazolyl,[15] piperazine, piperidine,[13] indole, indoline, carbazole and pyrazole[16] thiocarbamates together with their derivatives have been synthesized.

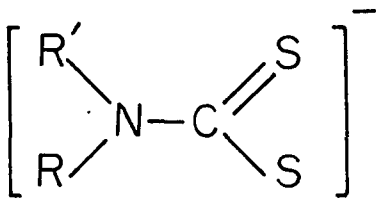
It has been noticed that antifungal activity of the various metal salts of dimethyl dithiocarbamic acid increases with increasing solubility. The sodium salt being the most active.[17]

Alkyl dithiocarbamates are very useful in agriculture and industry. In agriculture S-(benzyl) N, N-dialkyl dithiocarbamates are particularly effective against piricularia oryzae.[18] Thiocarbamates of the type RNHC-(:NH) $NH_2$. $4(S_2CNMe_2)_2$ were used as fungicides, microbiocides and algicides on tomatoes and apple trees.[19] In textile industry, dialkyl dithiocarbamates are used in stabilization and dyeing of the fabric. Dialkyl dithiocarbamates are frequently used as collectors for floatation of sulphides from finely milled ores.

Apart from their application in industry and agriculture, dithiocarbamates have achieved academic importance particularly owing to their dual nature of acting both as chelates and monodentate ligands.[20,21]

It has been established that splitting of  based on infrared spectrum near 1000 $cm^{-1}$ ± 70 occurs only when the

dithiocarbamato moiety is unsymmetrically bound, while the presence of only one band in 1000 $cm^{-1}$ region indicates a symmetrically bound dithiocarbamate group.[22-25] Further, there is splitting of $\alpha$-protons in p.m.r. spectrum of the metal dithiocarbamates at temperature as low as -70°C.[26] The splitting is never observed at room temperature because of the rapid exchange of the solvent. The substituents R and R' in dithiocarbamate group do not influence significantly the metal sulphur bonding.



Monosubstituted dithiocarbamates are less useful because of their reducing properties and tendency to decompose to hydrogen sulphide. The most important property of the dithiocarbamate ion is its decomposition to carbon disulphide and protonated amine.

Dithiocarbamates have been shown to coordinate with the tetrahalides of group(IV) elements[27] as well as with organometal (IV) halides.[28-31] An octahedral trans-configuration has been proposed for the bisdimethyltin dithiocarbamate, $Me_2Sn(SSCNMe_2)_2$.[23]

Innumerable novel transition metal adducts with a variety

of nitrogen donors have been characterised[32,33] but such a study with $R_3SnX$ is not extensive. The systematic study of $R_3SnX$ compounds is of interest because of two reasons namely, (i) due to their importance in biology, and (ii) in industry.

A study of the addition compounds of $R_3SnX$ with nitrogeneous ligands namely, acridine, piperazine, pyrrolidine, 1,10-phenanthroline and 2,2'-bipyridyl has been undertaken with varying size of rings and the number of nitrogen atoms to examine their effect on coordination. Poller and Toley[34] have studied 4,4'-bipyridyl adducts of tin(IV) chloride and organotin(IV) halides of the type $RnSnX_{4-n}$ where X = 1,2 or 3, found to have a trans octahedral geometry while for their 1:1 adducts a polymeric structure was suggested. A 1:1 adduct of pyrazine (1,4-diazine) with diphenyltin dichloride was also reported but its structure could not be proposed with certainty.

Antipyrine and 4-aminoantipyrine have also assumed importance because their salts have analgesic and antipyretic properties.[35,36] In a study to determine the site of protonation in antipyrine, the oxygen atom has been shown to be the most basic site. The infrared studies by Zaitsev and co-workers[37] on zinc and cobalt complexes of 4-dimethyl aminoantipyrine, $M(4Me_2aap)_2(NCS)_2$, indicated chelation through both CO and $NH_2$ groups which was later confirmed by Dick.[38] Antipyrine has two possible coordination sites, viz., oxygen and nitrogen and is expected to exhibit bidentate behaviour. However, it is ascertained that antipyrine strictly behaves as a monodentate ligand coordinating through the

oxygen atom only. A lowering in $\nu$(C=O) in the complexed ligand also showed that antipyrine is metallated through carbonyl oxygen.[39-41] This decrease is due to the reduction in $\pi$ bond character of C=O group on complex formation.

4-Amino antipyrine may coordinate in three ways: (i) through oxygen of the C=O group or (ii) the nitrogen of $NH_2$ group or (iii) through both oxygen and nitrogen atoms. Mostly the complexes of antipyrine with transition metal ions, viz., Mn(II), Co (II), Ni (II), Cu (II), Zn (II) and Cd (II) involve a chelated ligand and have octahedral geometry with halogen bridging.[39] Tetrahedral geometries are encountered with these ligands when antipyrine is used.

On the basis of the use of quinoline derivatives in the treatment of malaria, they assumed importance in the war periods. Even today the common antimalarial medicine Chloroquine is a derivative of quinoline called 7 chloro-4 (4-dimethylamino-1-methyl butyl) amino quinoline.[42]

Some of the derivatives of quinolines have been shown to have potential hypotensive activity in mammals.[43] Besides these pharmacological properties, the quinolines are also good Lewis bases. A study of their complexes with transition metal ions as well as with group(IV) metal halides have been reported.[44-48] However, no study seems to have been done on the interaction of organometal(IV) halides with the benzo quinolines, it was therefore of interest to study their interaction with organotin(IV) halides.

There is a variety of benzo quinolines namely, benzo(c)-, (f)-, (g)- and benzo (h) quinolines depending on the position of the benzene ring. In benzo (c)- and (f) quinolines, nitrogen is the only site for coordination while benzo (h) quinoline has the ability to form a new metal carbon σ bond through carbon atom at position 10, by abstraction of a proton in addition to the usual coordination of the nitrogen atom.[44,45] Benzo(h) quinoline has unusual property in the sense that its planarity will not allow the formation of a π-arene complex prior to the proton abstraction.

Dimeric complexes of benzo(h) quinoline with Pt(II) and Rh(III) through a proton abstracting process have been reported[44] formed. The compound with Pd(II) is pentacoordinated dimeric with halogen bridging while Pt(II) and Rh(III) complexes are monomeric. In some reported[45] complexes of benzo(h) quinoline the C–C σ bond has been retained. These include the compounds in which the bridging chlorine atoms have been exchanged for other anionic ligands or various neutral molecules. Such type of behaviour of benzo(h) quinoline has been exhibited in its complex with $PdCl_2$.

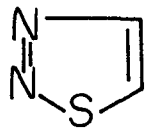
A variety of nitrogen and sulphur containing organic compounds have been used as ligands in the synthesis of various transition metal complexes. Many nitrogen and sulphur containing organic compounds have found use in medicine, industry and biology.

One of the common sulphur containing ligands whose interaction with metal ions has been examined in some detail is thiol.

The distinguishing property associated with the mercapto group is its ability to form complexes containing sulphur bridge. The mercaptide ions, $RS^-$ being highly polarizable, form strong bonds with typical class b metal ions.

Thiadiazole is a five membered heterocyclic ring system having one sulphur and two nitrogen atoms. Depending on the position of nitrogen atoms in the ring with reference to the sulphur atom numbered 1, there are three different thiadiazoles:

i) 1,2,3-thiadiazole
ii) 1,2,4-thiadiazole
iii) 1,3,4-thiadiazole



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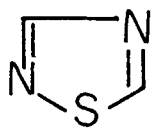

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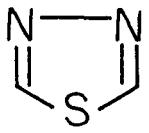
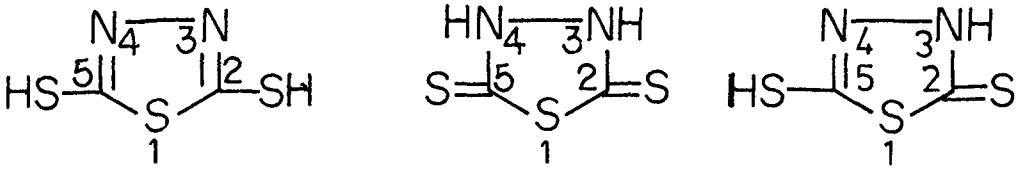


iii

2,5-Dimercapto-1,3,4-thiadiazole is a derivative of (III) in which the hydrogen atoms attached to the carbon atoms 2 and 5 are substituted by mercapto (-SH) groups. This compound is since long known to be a specific analytical reagent for bismuth[49] and is also called as bismuthiol I. It is also used in the analysis of several other metals.[50-52]

From a study of U.V. spectral studies it was suggested that bismuthiol I could exist in three tautomeric forms given below:



On the basis of chemical reactions it has been shown that this ligand exists in the mercapto form[53] but there is no spectroscopic evidence.

Bismuthiol I has been known to interact with various metals. Its complexes with Cu(II), Co(II), Ni(II) and Zn(II) have been noted. Amperometric titrations of copper and palladium and spectrophotometric determinations of palladium with this ligand have been made.[55-57] It is used in potentiometric titractions and solubility determination of silver salts.[58] Bismuthiol I finds several industrial applications. Its zinc compound is used as an oxidant for motor oil.[59] The tributyltin chloride compound of bismuthiol I is used as a protective agent against the attack of marine organisms on the bottom of the ships.[60] The Ni compound is used as a catalytic agent in the manufacture of acrylic acids.[61] The Co (II), Cu (II) and Zn (II) compounds have been used as bacteriocides.[54] It is also used in the manufacture of tetracycline,[62,63] which is low in chlorotetracycline. The physiology,

biochemistry and cytopathology of the cornea in relation to the injury by mustard gas and allied toxic agents have been examined. In this connection its effect on mammals was also examined but it was found to be very toxic due to the S–H groups.[64] It has been also used to form mercury derivatives which are intermediates in the manufacture of pharmaceuticals and insecticides.[65]

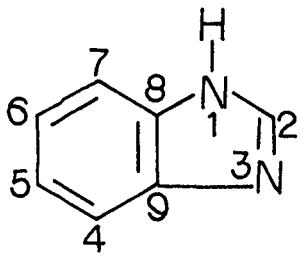
In view of the biological and industrial applications of bismuthiol I compounds, it was of interest to undertake the synthesis and characterization of its complexes with a few organotin (IV) halides.

The 2-benzimidazole thiol is also an industrially important compound. Certain metallic salts of 2-benzimidazole thiol have been used as heat stabilizers for polyamides.[66] It has been found useful as an antioxidant for rubber. Further, this compound has been used as specific reagent for the determination of various metals. The lead complexes of 2-benzimidazole thiol is also used in making photoconductive layers in electrophotographic plates.[67]

The adduct of this reagent with tin (II) and (IV) and antimony(III) halides have been reported by Ouchi and Takeuchi.[68] Rhodium and Iridium complexes have been isolated[69] and spectrophotometric determination of palladium using this compound has also been done.[70] The formation of Ru(III) complexes with 2-mercapto benzimidazole in an aqeous ethanol medium was studied by Pilipenko and co-workers spectrophotometrically.[71] The

applicability of this ligand provided the incentive to explore its ligation towards organotin (IV) halides.

The ring systems in which a benzene ring is fused to the 4,5-positions of imidazole is designated as benzimidazole.




Benzimidazole

Benzimidazoles possessing a free imino hydrogen are tautomeric systems. The two possible tautomeric forms of benzimidazole, possessing a plane of symmetry are identical and a definite assignment of the structure is possible. Mono- and poly-substituted benzimidazoles not possessing a plane of symmetry may behave as though they were composed of two compounds, thus rendering impossible a definite assignment of the structure. Substitution of the imino hydrogen eliminates the possibility for tautomerism and a definite assignment of structure becomes possible. The numbering starts at the substituted nitrogen. Benzimidazoles possessing substituents in the benzene portion will be referred to as benzimidazoles.[72]

Benzimidazoles are of immense importance because of their applications in medicine and biology.[72] These are useful as growth inhibitor of certain yeasts and bacteria. Vitamin $B_{12}$

may be regarded as a derivative of 5,6-dimethyl benzimidazole. The imidazole nucleus is known to coordinate readily with a number of metallic ions and this characteristic enables it to play an important role in vitamin $B_{12}$ and haemoglobin. Benzimidazole has also been reported to inhibit the production of a variety of viruses in tissue cultures. Alkyl substituted benzimidazoles in particular have shown to inhibit the multiplication of influenza virus. The alkylaminomethyl and 2-diallyl amino methyl-benzimidazoles possess a local anesthetic activity. The relative activities of these compounds appear to be dependent on the nature and size of the allyl groups present.

# CHAPTER II

## EXPERIMENTAL METHODS

## EXPERIMENTAL METHODS

Several physico-chemical methods are available for structure elucidation of coordination compounds. The techniques used for the investigation of the structure of newly synthesised compounds described in the present work are infrared spectroscopy and molar conductance measurements.

It seems therefore, appropriate to give a brief description of these techniques.

### Infrared Spectroscopy

Infrared spectrum arises from the different modes of vibrations and rotation of a molecule. The pure rotational spectrum of molecules occur at a very long wave-length in the microwave region well beyond the wave length limit of about 25 μ. At wave-length below 25 μ the radiation has sufficient energy to cause changes in the vibrational and of course also the rotational levels of molecule.

According to the quantum theory there are discrete energy states, both rotational and vibrational in which each molecule can exist. For diatomic, linear poly atomic, and spherical top molecules the energy of rotational levels is given by the equation:

$$E_r = \frac{J(J+1)h^2}{8\pi^2 I} \qquad (1)$$

where $J$ is the rotational quantum number which can have any integral value, 0, 1, 2, 3, —— and I is the moment of intertia of the molecule above the axis of rotation.

For the symmetrical and asymmetrical molecules the formula is somewhat more complex. Transitions between the different rotational levels in the microwave and infrared regions are governed by the selection rule

$$\Delta J = \pm 1$$

If a molecule is raised from an energy state with a quantum number $J$ to that with quantum number $J + 1$, the energy involved will be

$$h\nu = \Delta E = E_{(J+1)} - E_J \qquad (2)$$

from which the frequency of energy absorbed in wave numbers can be obtained by substitution of equation (1) in equation (2) as follows:

$$\nu_c = \frac{h(J+1)}{4\pi^2 IC} = 2B(J+1) \qquad (3)$$

where B, the rotational constant, is equal to $h/8\pi^2IC$. The pure rotational spectrum then would consist of equally spaced lines. The constant frequency separation between successive lines being equal to 2B, i.e., to $h/4\pi^2IC$ $cm^{-1}$. It is observed that as the moment of inertia I increases, the frequency of the rotational lines for a given I value, decreases. For relatively

heavy or large molecules, the pure rotational spectrum will thus appear in the very far infrared region.

In the infrared region below 25 μ changes in the vibrational states of the molecule occur during absorption of radiation for small amplitude of vibration, the vibration may be considered harmonic and the energy of the vibrational quantum level is given by eqn. (4).

$$E_V = h\omega ( v + 1/2) \qquad (4)$$

where $\omega$ is the fundamental vibrational frequency of the harmonic oscillator, and $v$ is the vibrational quantum number which can have any integral value, 0, 1, 2, 3 .... The difference in energy between successive energy levels of the harmonic oscillator is thus always $h\omega$.

In order that a vibrating molecule should interact with the fluctuating electrical field of electromagnetic radiation the molecular electrical dipole moment must change its magnitude or orientation with respect to a fixed coordinate system during the motion. It is the magnitude of this change of dipole moment which determines the intensity of a transition. There are 3N-6 normal vibrations of a non-linear molecule of N atoms and hence the 3N-6 frequencies associated with them are called fundamental frequencies of the molecule. From the symmetry that a molecule possesses one can determine how many of the 3N-6 vibrations will be observed in its infrared spectrum, and conversely, from the infrared spectrum the molecular symmetry may be deduced. A

vibration will be infrared active if its symmetry species is the same as that of at least one of the dipole moment components. For harmonic oscillators, transitions between the various energy levels are governed by the selection rule $\Delta V = \pm 1$. In actual fact, the purely harmonic conditions do not prevail for real molecules. The frequent observation of overtones and combination tones of these vibrations corresponding to change $\Delta V = 2,3$, etc., is a consequence of the anharmonic nature of the normal modes. These additional bands are usually very much weaker than the parent fundamentals.

For harmonic oscillation of frequency $\omega$ is related to the force 'f' binding the vibrating groups together and the reduced mass $\mu$, by the relationship

$$2\pi\omega = \left(\frac{f}{\mu}\right)^{1/2}, \quad \mu = \frac{m_A \, m_B}{m_A + m_B} \qquad (5)$$

where $m_A$ and $m_B$ are the masses attached to either of the vibrating system. In terms of the frequency $\nu_V$, in wave numbers, eqn. (6) becomes

$$\nu_V = \frac{1}{2\pi C}\sqrt{f/\mu} \qquad (6)$$

Thus the frequencies of vibration of a molecule are related to the masses and binding forces. In many of the normal modes of vibrations of a molecule the main participants in the vibration are two atoms held together by a chemical bond. The frequencies are only slightly affected by another atom, attached to the atoms

concerned, and thus these vibrational modes are characteristic of the group in the molecule and are very useful in identifying a compound, especially in deducing the structure of an unknown compound or substance. In this work only those frequencies which are pertinent to the discussion of the newly synthesized compounds will be discussed.

N-H Stretching Vibrations

The N-H stretching vibrations occur in the region 3500-3300 $cm^{-1}$ in dilute solutions.[73] Primary amines in dilute solutions of non-polar solvents give two absorption bands in this region. The first which is due to symmetric stretch is usually found near 3500 $cm^{-1}$ and the second which arises from the corresponding asymmetrical mode is found near 3400 $cm^{-1}$. The position and intensity of both these bands are sensitive to substitution. Secondary amines show only a single N-H stretching absorption in dilute solution in the above mentioned region. The intensity and frequency of N-H stretching vibrations of secondary amines are very sensitive to structural changes. The band is found in the range 3350-3310 $cm^{-1}$ (low intensity) in aliphatic secondary amines, and near 3490 $cm^{-1}$ (much higher intensity) in heterocyclic secondary amines such as pyrrole and indoles. Fluorine substitution generally seems to enhance the intensity of the band. Ring strain seems to have little effect on N-H stretching vibration as can be seen by the values of ethyleneimine (3367-3341 $cm^{-1}$) and diethyl amine (3384 $cm^{-1}$).

The N-H stretching absorption shifts to lower values in the solid state due to extensive hydrogen bond. At a very low concentration pyrrolidine shows a band at 3367 $cm^{-1}$ due to the monomeric N-H stretching frequency.[74] As the concentration increases, a new band appears at 3268 $cm^{-1}$ due to intermolecular association (N-H —— N bonding). The intensity of the low frequency band increases with increasing concentration until complete association occurs in the liquid state. Hydrogen bonding is very common in ureas and thioureas.[75] In concentrated solutions of thioureas in $CCl_4$ and $CHCl_3$ two to four bands in the 3500-3300 $cm^{-1}$ region are present. The highest frequency band is much sharper than any of the others, the broadness of which can reach 200 $cm^{-1}$. Further, the molar extinction of the highest frequency band increases with decreasing concentration, the trend being opposite for the other bands. In very dilute solutions only the highest energy band is visible. There is always in the solid spectra, however, a strong broad band together with weaker and narrower bands on the lower frequency side. This suggests a strongly associated condition for thioureas in the solid state.

Valuable informations have been obtained on the structure and tautomerism of many heterocyclic molecules and their substituted derivatives from a study of the N-H stretching absorption. The $\alpha$ and $\gamma$-mercaptopyrimidines and other mercapto-aza-aromatic compounds exist in the thione form, both in the solid state and in solvents of low polarity.[76] In the solid state a weak band in the range 3160-3190 $cm^{-1}$ is regarded as

evidence for the presence of -NH group. In solution a broad band is found in the range 3350-3420 $cm^{-1}$, due to N-H stretching in unassociated molecules (weaker bands also appear at lower frequencies, due to associated molecules).

The IR spectra of 2- and 4-hydroxypyrimidines in the solid state and in $CHCl_3$ solution give absorption bands due to N-H bond stretching vibrations, indicating their existence in the tautomeric Keto form.[77] However, aminopyrimidines, generally exist in the tautomeric form, and in solution ($CHCl_3$, $CCl_4$) give two bands characteristic of amino group.[78,79]

N-H Deformation Vibrations

For the deformation frequencies of the $NH_2$ group in primary amines four characteristic peaks should appear, but the only definite assignment has been done in the case of scissoring vibration, generally observed in the region 1650-1590 $cm^{-1}$.[80] The lower frequency deformation vibration of the $NH_2$ group has not been investigated in detail. The $NH_2$ twisting, wagging and torsional vibrations in methylamine have, however, been assigned to 1455, 780 and 264 $cm^{-1}$ respectively. Secondary aliphatic amines show an extremely weak band in the range 1650-1550 $cm^{-1}$ due to N-H deformation vibration and it is difficult to detect this band readily. The assignment of this vibration is very difficult in case of aromatic amines because of the presence of aromatic ring vibrations in this region.

C-H Stretching Vibrations

These vibrations are usually observed in the 3100-3000 $cm^{-1}$ region in carbocyclic and heterocyclic systems.[74] Some aromatic compounds give rise to three bands near 3038 $cm^{-1}$. Pyridine shows C-H absorption in the range 3070-3020 $cm^{-1}$ which appear as a series of multiple absorptions under high resolution.[81] In pyrimidines this band is observed near 3050 $cm^{-1}$. A weak band is observed in the case of trisubstituted pyrimidines, since only one free ring hydrogen atom is present. This band is absent in tetra substituted pyrimidines.

C-H In-Plane and Out-of-Plane Deformation Vibrations

A number of characteristic absorption bands in the region 1250-1000 $cm^{-1}$, exhibited by most of the heterocyclic compounds are attributed to C-H in-plane deformation and the ring breathing modes.[74] In diazines these bands are observed in the range 1239-1021 $cm^{-1}$.[82] Bands appearing in the region 900-700 $cm^{-1}$ have been attributed to the C-H out of plane deformation vibrations, and the position of these bands depend on the number of free hydrogen atoms adjacent to one another.

S-H Stretching Vibrations

The S-H stretching vibrations in mercaptans are usually observed in the range 2600-2550 $cm^{-1}$.[83] The S-H absorption is not inherently strong, and is often difficult to detect in dilute solutions or in samples examined in very thin cells. It

is also observed in compounds containing -COOH groups which exhibit general absorption in this region. However, if allowance is made for these factors, the presence or absence of a band in this region can afford decisive evidence for the occurrence of a mercapto group.

Simple mercaptans such as propyl, butyl and isoamyl mercaptans give a well defined but rather weak absorption at 2650-2550 $cm^{-1}$. Randell et al.[84] proposed the range 2688-2560 $cm^{-1}$ for the S-H band, but this is clearly designed to include hydrogen sulphide which has its asymmetric S-H mode at 2688 $cm^{-1}$. This is an exceptional case, and aromatic mercaptans do not appear to absorb at frequencies higher than 2600 $cm^{-1}$, Sweeney et al.[85] have shown that 1,2-dimercaptoethane absorbs at 2350 $cm^{-1}$ in the liquid state, but this appears to be wholly exceptional. Thus even thioacetic acid (2550 $cm^{-1}$) and dithioacetic acid (2481 $cm^{-1}$) absorb at higher frequencies, indicating that polymerisation does not occur to any extent, and indeed the S-H link is not apparently capable of the extensive degree of hydrogen bonding which occurs with -OH and -NH groupings. There is very little change in the frequency of S-H absorptions on passing from the liquid state to dilute solutions, so that any intermolecular bonding effects must be very small. On the other hand, small shifts suggestive of hydrogen bonding have been observed in solution in certain bases and other compounds, indicating the formation of a weak S-H---N bonds. Thiophenol is capable of hydrogen bonding to sulphoxides to give a frequency shift of the S-H vibration of

100 $cm^{-1}$, however, with aryl sulphoxides the shift is somewhat smaller.

Studies in this region have been used to determine whether certain hetero aromatic mercapto compounds exist in the mercaptan or thio keto form.[76-86] The absence of any S-H absorption from the spectrum of mercapto benzothiozole is one of the strongest pieces of evidence for the existence of this substance as a thio-ketone under normal conditions. 3-Mercaptopyridine and 8-mercapto quinoline exist in the mercapten form in solvents of low dielectric constant.[76] The broad and weak band at 2520 $cm^{-1}$ in the spectrum of 8-mercapto quinoline (for which there is no counterpart in the spectrum of 8-methylthioquinoline) is attributed to S-H stretching; there is probably some intermolecular hydrogen bonding between the -SH group and the vicinal nitrogen atom.

C=N Stretching Vibrations

A band of variable intensity in the region 1690-1640 $cm^{-1}$ is attributed to C=N stretching vibrations in open-chain systems or in non-conjugated ring systems.[87] With conjugated cyclic systems the position is much less clear, and the C=N absorptions have been assigned as being within the range 1660-1480 $cm^{-1}$. In cyclic compounds and cyclic materials without internal conjugation the C=N absorption is assigned to the 1650 $cm^{-1}$ region. The C=N absorption band occurs near 1667 $cm^{-1}$ region in oxazines, oxazolines, oximes and imines. However, the C=N absorption bands are difficult to identify for two reasons. First owing to

the considerable changes in intensity which follow changes in its environment, and secondly because information available on the effects of conjugation in ring systems is often conflicting and indecisive.

C-N Stretching Vibrations

The C-N stretching absorptions give rise to strong bands in the region 1360-1250 $cm^{-1}$ in aromatic amines.[73] In aliphatic amines the absorptions are in the 1220-1020 $cm^{-1}$ range and are often of low intrinsic intensity. In aromatic primary amines there is one band in the region 1340-1250 $cm^{-1}$ but in secondary amines two bands have been observed in the region 1350-1280 $cm^{-1}$ and 1280-1230 $cm^{-1}$. The position of C-N absorption does not differ much from C-C absorption, but the intensity is relatively large because of C-N polarity.

Ring Stretching Vibrations

Characteristic aromatic ring vibrations appear in the region 1600-1350 $cm^{-1}$ in the most of the heterocyclic compounds.[74] The position and intensity of these vibrations are dependent on the nature of the ring and type of substitution. Six membered ring show four bands around 1605, 1575, 1480 and 1430 $cm^{-1}$, whereas five membered rings show three bands around 1590, 1490 and 1400 $cm^{-1}$. The intensities of these bands give an idea of the pattern and nature of substitution in the ring. Thus in 4-substituted pyridine-1-oxides and 3-substituted pyridines the intensity of

the band around 1605 $cm^{-1}$ is high for both electron-withdrawing and electron-donating substituents, whereas in the case of 2- and 4-substituted pyridines and 3-substituted pyridine-1-oxides, the intensity is high with electron donor groups and low with electron acceptor groups. The intensity of the band at around 1575 $cm^{-1}$ also shows similar variations with substitution. Electron donating substituents increase the intensity of the band around 1480 $cm^{-1}$, whereas the band near 1430 $cm^{-1}$ is unaffected by the nature of the substituents. This particular trend in the change of intensities has been explained as being due to the charge disturbances in the molecule.

The characteristic pattern of absorption of the ring stretching vibrations result from the complete interaction of the C=C, C=N and or N=N vibrations (e.g., in 1,2-diazine) and it is, therefore, very difficult to isolate the different vibrations. This is due to the fact that the lone pair of electrons on the nitrogen atom will be able to conjugate with the ring, the magnitude of which depends on the coplanarity of the system. Therefore, these vibrations are sensitive to minor alterations in molecular geometry and are difficult to distinguish from other vibrations. Even though a band of variable intensity in the region 1660-1630 $cm^{-1}$ is attributed to C=N stretching in open-chain $\alpha,\beta$-unsaturated compounds in cyclic conjugated systems the appearance of bands in this region can only be attributed to the ring stretching modes.

Substituted pyrimidines, generally, show four bands in the

1590-1375 $cm^{-1}$ region,[82,88-90] which is probably due to $NH_2$-deformation mode. The hydroxy pyrimidines are also not suitable for the development of correlations for ring vibrations of this type, as they may act in the tautomeric keto form, in which the double bond absorptions of the ring would be expected to be different from the fully aromatic systems.

C=O Stretching Vibrations

The C=O stretching vibrations of various carbonyl groups absorb in the region 1900-1600 $cm^{-1}$.[91] A more specific range is defined by the type of carbonyl (e.g., ketones, esters, etc.), and the position is further affected by a variety of effects. The frequency of the carbonyl absorption is determined almost wholly by the nature of its immediate environment, and the structure of the rest of the molecule is of little importance unless it is such as to give rise to chelation or some similar effect. Thus, the carbonyl shifts away from the normal position in $\alpha,\beta$-unsaturated materials and in carbonyl compounds with strongly electronegative substituents on the $\alpha$-carbon atom, whilst in cyclic ketones the frequency shift and its direction are related to the degree of strain of the ring. Frequency shifts due to chelation and to mutual interference effects can also be considerable in some cases. However, in each of these cases the extent of the frequency shift to be expected is known and the new range of frequencies falls within comparatively narrow limits.

A carbonyl group situated between two methylene groups represents the simplest case of an undisturbed C=O stretching vibration. Studies by many workers have shown that in solution the frequency of the carbonyl absorption of simple ketones of this type always lies within the narrow range 1725-1706 $cm^{-1}$, provided that no hydrogen bonding or other interference effects occur.[92] Carbonyl groups in unstrained saturated rings absorb within the same overall frequency range 1720-1706 $cm^{-1}$.

The physical state has a direct effect on the carbonyl frequency. Acetone, for example, absorbs at 1742 $cm^{-1}$ in the vapour phase, whereas in solution the frequency lies between 1728 $cm^{-1}$ and 1718 $cm^{-1}$, depending on the solvent. Similarly dodecyl ketone absorbs at 1740 $cm^{-1}$ in the vapour state, and between 1724 $cm^{-1}$ and 1717 $cm^{-1}$ in solution. It is probable that some form of dipolar association is occurring in the condensed phase, resulting in a low frequency shift of the order of 20 $cm^{-1}$ conjugation of a carbonyl group with a C=C linkage results in a lowering of the frequency by an amount depending on the nature of the double bond. An aliphatic C=C bond in conjugation with a carbonyl group reduces its frequency by about 40 $cm^{-1}$ and the absorption occur in the range 1685-1665 $cm^{-1}$. When an aryl group is directly attached to the carbon atom of the carbonyl group, the frequency shift of the carbonyl is less than that occurring with a full double bond in conjugation, and the absorption band occurs in the range 1700-1680 $cm^{-1}$, with two aryl groups directly attached. However, there is a further fall

in the frequency to 1670-1660 $cm^{-1}$. The influence of an $\alpha$-aryl group is additive with that of any other structure which is capable of influencing the C=O frequency. With a six membered ring C=O with an $\alpha$-aryl group, the frequency is found to be 1695-1686 $cm^{-1}$ which is the same as with similar open-chain materials. With a five membered ring C=O, however, the frequency increases to 1715-1706 $cm^{-1}$, the strain of the five membered ring being offset to some extent by the aromatic conjugation. Halogen substitution in the immediate vicinity of carbonyl group results in a high frequency shift of the carbonyl absorption. This is particularly marked in the acid chlorides where a chlorine is directly attached to the carbonyl group, but there is still an appreciable effect when the halogen is situated on the $\alpha$-carbon atom. Thus $\alpha$-propionic acid, for example, absorbs at 1730 $cm^{-1}$ as against 1710 $cm^{-1}$ for $\beta$-chloropropionic acid.

When intramolecular hydrogen bonds are formed, the carbonyl absorption bands may be lowered by 50 $cm^{-1}$ according to hydrogen bond strength.[91] 1-Hydroxyanthraquinone shows two C=O bands at 1680-1675 $cm^{-1}$ and 1630-1622 $cm^{-1}$, corresponding to free and bonded carbonyl groups. With two hydroxyl groups in each of the $\beta$-positions only one band is shown at 1639-1623 $cm^{-1}$, whilst in the extreme case of 1,4,5,8-tetra hydroxyanthraquinone the carbonyl frequency has fallen to 1525 $cm^{-1}$. Similarly fumaric acid absorbs at 1680 $cm^{-1}$, in contrast to the normal value of 1705 $cm^{-1}$ of maleic acid. Salicylic acid absorbs at 1655 $cm^{-1}$

which is comparable with the shifts experienced in the case of the $\alpha$-hydroxy-$\alpha,\beta$-unsaturated ketones. 3-Amino-2-naphthoic acid absorbs at 1665 $cm^{-1}$.

Amides generally show a strong absorption band near 1640 $cm^{-1}$ when examined in the solid state.[92] The fact that the absorption is at an appreciably lower frequency than the carbonyl absorption of normal ketones must be due to the effect of resonance with the ionic form. This is enhanced by the strong association effects in the solid state and the corresponding vapours absorb at considerably higher frequencies. The amide first absorptions is subject to a considerable alteration on change of state in which hydrogen bonding is broken, and is also liable to variations in solution depending on the polarity of the solvent employed. Thus hexanamide absorbs at 1655 $cm^{-1}$ in the solid state, at 1668 $cm^{-1}$ in concentrated solutions and at 1680 $cm^{-1}$ in dilute chloroform solution. The corresponding values of 1692 $cm^{-1}$ and 1672 $cm^{-1}$ given for this absorption band in dioxane and in methanol indicate the degree of frequency shifts likely to be associated with alteration in the type of solvent employed. The carbonyl absorption of N-ethyl-acetamide ranges from 1687 to 1663 $cm^{-1}$ over a series of solvents, even at concentrations at which hydrogen bonding effects are precluded. At higher concentrations the frequency varies continuously with the concentration due to change in strengths of the intermolecular hydrogen bonds. Formamide absorbs at 1740 $cm^{-1}$ as vapour and at 1709 $cm^{-1}$ in dilute chloroform solutions. Therefore, carbonyl frequencies

are much closer to those of ketones and suggest that the contribution of the ionic form is quite small under these conditions.

N,N-disubstituted amides are incapable of forming hydrogen bonds, and the carbonyl absorption band is consequently not much influenced by changes in physical state. In these cases the amide first band usually falls near 1650 $cm^{-1}$ unless a phenyl group is substituted on the nitrogen atom, when it is raised to 1690 $cm^{-1}$. This is due to the competitive effect of the ring for the lone pair electrons of the nitrogen ring. In consequence the contribution of the ionic form of the amide is reduced and the carbonyl frequency is raised. A similar effect may account for the high frequencies shown by N-nitrosoamides, which absorb near 1740 $cm^{-1}$ in solution. The inverse effect occurs in dimethyl urea, in which the ionic character of the carbonyl is reinforced by the second nitrogen atom so that in the solid state the frequency falls to 1610 $cm^{-1}$.

Infrared studies have[90,93-99] shown that a large number of $\alpha$-and $\gamma$-hydroxy-aza-aromatic derivatives are amides both in solid state and in solution. A very strong band in the range 1620-1750 $cm^{-1}$ shows the presence of a CO group. 2-Hydroxypyrimidine and the 4-isomer in the solid state and in solution show absorption bands in the 1600-1700 $cm^{-1}$ region which have no counterpart in the spectra of the methoxy derivatives and must be due to the C=O bond stretching vibrations. Thus these compounds in the states examined exist predominently in the amide form.

C=S Stretching Vibration

The identification of the position of the C=S absorption has been a matter of some difficulty. In carbon disulphide the C=S stretching modes have been assigned to 1522 $cm^{-1}$ and 650 $cm^{-1}$, whilst in carbonyl sulphide it is given at 859 $cm^{-1}$.[83] These are unusual cases in which the carbon is doubly unsaturated, and they do not offer any guidance to the likely position of the C=S vibration in saturated thioureas and similar compounds. Preliminary calculations indicated that the ratio C=O/C=S would be about 1.5 and that the C=S frequency would be found in the 1200-1050 $cm^{-1}$ region. Just as is the case with the carbonyl group, the C=S absorption is found to be sensitive to the nature of the surrounding structure but the relative effects of various substituents are not always the same, and the ratio between the carbonyl and thiocarbonyl frequencies varies over the range 1.6 to 1.14.

Systematic correlations of the available data on thiocarbonyl stretching frequency indicate that when it is unambiguously identifiable, e.g., in $(-CH=CH-)_2$, C=S and -CS-SR derivatives, it is at 1190 ± 70 $cm^{-1}$.[100,101]

However, in some molecules, notably thioamides and thioureas, the thiocarbonyl stretching frequency is uncertain, as there is complete mixing between the C=S stretching mode and other vibrations of similar frequencies.[102,103] This frequency is hardly susceptible to polar effects. It has been calculated[104]

that the C=S stretching frequency in thioformaldehyde should be 1120 ± 40 $cm^{-1}$, while in thiocarbonyl chloride, it is at 1120 ± 40 $cm^{-1}$. By contrast, the carbonyl stretching frequency in carbonyl chloride (1827 $cm^{-1}$) is considerably higher than that in formaldehyde (1744 $cm^{-1}$). Presence of thiocarbonyl stretching frequency in mercapto compounds, provides a direct evidence for their existence in the thioamide form. Spinner[104] observed an intense band in the range 1100-1190 $cm^{-1}$ in several $\alpha$- and $\gamma$-mercaptoaza-aromatic compounds attributable to C=S stretching frequency indicating them to be in the thioamide form. There has been great uncertainty with regard to the assignment of the C=S stretching frequency in nitrogen containing compounds and the assignments[105] in these compounds vary in the wide range of 850-1570 $cm^{-1}$. Elmore[106] has shown that the band which is generally assigned to C=S stretching vibration in such compounds results from the coupling of the C-N and C=S stretching vibrations. Normal coordinate analysis of N-methylthio formamide, N-methylthioacetamide, N,N'-dimethylthiourea and tetramethyl-thiourea[107,108] shows clear evidence for vibrational mixing in these compounds. In secondary thioamides the bands with considerable contribution from the C=S stretching vibration[109] are found in the region 670-700 $cm^{-1}$. This is considerably lower than in simple thiocarbonyl compounds, where the C=S vibration is localised. In thioureas, two bands in the region 1080-730 $cm^{-1}$ are found to have appreciable contribution from the C=S stretching vibration.[102] Sumuki's calculations[108] show

that the 843 $cm^{-1}$ band for $HCSNH_2$ correspond to an almost pure C=S mode and the intrinsic frequency of the C=S vibrations vary from 900 to 850 $cm^{-1}$. Gosavi et al.[107] performed a normal coordinate analysis on N,N'-dimethylthiourea and tetra methylthiourea and assigned various mixed C=S stretching frequency bands. The mixed vibration bands of N,N'-dimethylthiourea have the contribution from C=S stretching vibrations as: 1504 $cm^{-1}$, 10 %; 1420 $cm^{-1}$, 18 % and 752 $cm^{-1}$, 83 %. Similarly, in tetramethylthiourea the contribution from C=S stretching vibrations is as: 1408 $cm^{-1}$, 25 %; 1013 $cm^{-1}$, 50 %; 990 $cm^{-1}$, 50 % and 462 $cm^{-1}$, 37 %. Since the force constants $f_{CN}$ and $f_{CS}$ are quite similar, the major contributions from C-N and C=S vibrations are found in the bands which are quite close to each other (e.g., 850 and 752 $cm^{-1}$ in N-N'-dimethyl thiourea). The mixed vibration bands are in the regions of so-called N-C=S bands.[109]

C-S Stretching Vibrations

The C-S stretching frequency generally appear as a band of weak or moderate intensity in the range 720-570 $cm^{-1}$. In the Raman spectra this band is very strong. There appears to be a progressive decrease in the frequency in the order: primary, secondary and tertiary C-S. In aromatic derivatives the C-S frequency is found towards the top of this range and some difficulty is experienced in recognising the C-S frequency due to the presence of the intense CH-out-of-plane deformation band in this region. In phenyl sulphonyl halides the C-S vibration is

found between 715 and 706 $cm^{-1}$. In aromatic thiocyanate it appears in the region 740-680 $cm^{-1}$. In thioketols, broad bands with several maxima are found probably due to vibrational coupling.

## M-S Stretching Vibrations

The metal sulphur stretching frequency is of particular interest as it gives a direct evidence for coordination through the sulphur atom. It appears in the low frequency region, viz., 480 to 210 $cm^{-1}$ range.[110] In many instances two bands are observed, one of medium to strong intensity, and a weaker band at a frequency 10 to 40 $cm^{-1}$ lower than the stronger band. The Sn-S frequencies earlier reported appear in this range.

## Metal-halogen Vibrations

Metal-halogen vibrations which appear in the low-frequency infrared region, are quite useful in determining the stereochemistry of coordination compounds. In a tetrahedral $MX_4$ molecule ($T_d$) there are four normal modes of vibration. All the four vibrations are Raman active, whereas only two ( $\nu_3$, , $\nu_4$) are infrared active, and their position depends upon the mass of the metal and halogen.[111] For an octahedral $MX_6$ molecule ($O_h$) (e.g., $GeCl_6^{-2}$, $SnCl_6^{-2}$, etc.) there are six possible normal modes of vibration. Three ( $\nu_1$, $\nu_2$ and $\nu_5$) are Raman active whereas only two ( $\nu_3$, $\nu_4$) are infrared active.[112] In Octahedral ions ($GeX_6^{-2}$, $SnX_6^{-2}$, etc.) the M-X vibrations are found at lower

frequencies than those found for similar vibrations in a tetrahedral environment. When metal tetrahalides, $MX_4$, form octahedral complexes, $MX_4.2$ donor, the M-X stretching vibrations by analogy with these octahedral ions, are considerably shifted to lower frequencies[113-117] relative to those of the free tetrahalides. In many addition compounds metal-halogen vibrations are much more intense than ligand vibrations. In group IV, this is most marked for adducts of tin tetrahalides and least marked for adducts of silicon tetrahalides where intensities are frequently comparable. Ligands may occupy either cis or transpositions in the octahedron. The use of infrared spectroscopy in the far IR region to study the cis-trans isomerism of the adducts of type $MX_4.L_2$ (where M = tin silicon or germanium, X is halogen and L is a monodenatate ligand) has been out-lined by many workers.[115-124] Neglecting the coupling between the M-X and the ligand vibration, the trans-adduct is considered to be similar to a perturbed square planar $MX_4$ unit, so that only one infrared active fundamental M-X stretching vibration ($E_u$ symmetry) is predicted,however, for the cis-configuration there would be at least two fundamentals.[115] There are numerous flaws in this simple approach. Fermi resonance may make a combination band intense enough to be accepted as a fundamental. Alternatively, certain fundamentals may be very weak, as for gaseous antimony trichloride, whose $a_1$ fundamental is very very strong relative to the weak e fundamental. Accidental degeneracies may occur or

bands may be unresolved. Electronic transanctions and lattice vibrations may appear. Calcium fluoride, for example, has a broad infrared absorption band at about 270 $cm^{-1}$. Crystal-field effects may resolve degeneracies, thus one triply degenerate $f_{1u}$ fundamental of symmetrical Si $F_6^{-2}$ is resolved into two peaks in the crystalline compound $BaSiF_6$, probably owing to elongation of the octahedron along the three fold axis, causing a lowering of the symmetry from $O_h$ to $D_{3d}$.

Beattie and co-workers[125] carried out a normal coordinate analysis of the octahedral species cis- and trans- $MX_4L_2$ by Wilson's F-G matrix method, and calculated vibrational frequencies for coordination compounds of some tetrahalides of Group (IV). The calculations show that for a cis-adduct three high frequency bands are to be expected, the next nearest band lying considerably below this group (all the bands are infrared and Raman active). In the case of the trans adducts if the metal-ligand force constant is low compared with the metal-halogen, there will be one main band in the same region as the set of three absorptions mentioned for the cis-adducts. However, where the metal-ligand force constant is low compared with the metal-halogen, there will be one main band in the same region as the set of three absorptions mentioned for the cis-adducts. However, where the metal-ligand force constant is high, the $e_u$ and $a_{2u}$ vibrations (both IR active) will occur in similar regions of the spectrum. Thus in a crystalline compound, crystal-field resolution of the $e_u$ vibration to doublet, plus the presence of an $a_{2u}$ vibration could

lead to a spectrum similar to that of a cis-adduct. The $e_u$ vibration (anti symmetric stretch) is relatively insensitive to the value of $f_{M-L}$ and also to the value of the bending force constants. Thus, identification of cis- and trans-isomers by infrared spectroscopic examination is helpful in favourable cases, particularly when solution spectra canbbe obtained.

Metal-ligand Vibrations

The metal-ligand stretching frequency is of particular interest since it provides direct information regarding the coordinate bond. It appears in the low frequency region and depends on the following factors:

1. Mass of the metal and ligand.
2. Oxidation number of metal ion.
3. Coordination number of metal ion.
4. Geometry of the complex.
5. Basicity of the ligand molecule.
6. Bridging or non-bridging anions.
7. Ligand-field stabilisation energy.

Sn-C Stretching frequencies

I.R. spectroscopy is quite valuable as it provides information on the configuration of organotin compounds. Particularly important is the criterion established for determining the configuration of $SnC_3$ and $SnC_2$ moieties in trimethyltin and dimethyltin derivatives.[126] If the spectrum reveals two Sn-C stretching vibrations (both the symmetric and the asymmetric modes), the configuration of $SnC_3$ group is non planar or that of

$SnC_2$ is non linear. However, if there is only one band assignable to an Sn-C stretching vibration, the configuration of $SnC_3$ group is planar or that of $SnC_2$ is linear.[127] This criterion has been further supported by X-ray studies.

## Molar Conductance

The conductivity measurement is one of the simplest and easily available technique used in a research laboratory, for the characterisation of coordination compounds. It gives direct information regarding whether a given complex is ionic or covalent, i.e., whether the anions satisfy the primary or the secondary valency of the metal ion in a coordination compound. Several studies of molar conductivities[128-140] of different kind of electrolytes in different solvents are now available and it is useful to compare molar conductance ($\Lambda_m$) value of a given complex with that of the similar electrolyte. Conventionally solution of $10^{-3}$ M strength is used for the conductance measurements. Molar conductance values for different type of electrolytes in nitrobenzene at this concentration are as 1:1, 20-30; 2:1, 50-60; 3:1, 70-82; 4:1, 90-100 $Ohm^{-1}$ $cm^2$ $mole^{-1}$.[136]

A good description of electrolytic behaviour of coordination compounds in various organic solvents is given in a review.[136] Molar conductance values for complexes of the various electrolyte types of $10^{-3}$ M concentrations in nitro methane are as 1:1, 75-95; 2:1, 150-180; 3:1, 220-260; 4:1, 290-330 $Ohm^{-1}$ $cm^2$ $mole^{-1}$.

Reference values for non-complex electrolytes lead to an average $\Lambda_m$ value for 1:1 electrolytes of ~91.5 $ohm^{-1}\ cm^2\ mole^{-1}$. However, the values for the tetraphenylborate and tetra-isoamyl-borate salts are very low because of the low ionic mobilities and if these values are excluded from the overall average, a value of ~96 $ohm^{-1}\ cm^2\ mole^{-1}$ is obtained. Average values for complexes of unidentate ligands are for 1:1 electrolytes 88.5 $ohm^{-1}\ cm^2\ mole^{-1}$ and for 2:1 electrolytes 167 $Ohm^{-1}\ cm^2\ mole^{-1}$. For the whole range of complexes which has been studied, values claimed for 1:1 electrolytes range from 60-115 $ohm^{-1}\ cm^2\ mole^{-1}$, with an average value of ~83 $ohm^{-1}\ cm^2\ mole^{-1}$. For 2:1 electrolytes, values claimed cover the range 115-250 $ohm^{-1}\ cm^2\ mole^{-1}$, an average value being 168 $ohm^{-1}\ cm^2\ mole^{-1}$. Values as low as 180 $ohm^{-1}\ cm^2\ mole^{-1}$ and as high as 300 $ohm^{-1}\ cm^2\ mole^{-1}$ have been given for 3:1 electrolytes. A reasonable average value is 242 $ohm^{-1}\ cm^2\ mole^{-1}$. For 4:1 electrolytes (115-118), values cover a range 244-341 $ohm^{-1}\ cm^2\ mole^{-1}$ with an average value of 307 $ohm^{-1}\ cm^2\ mole^{-1}$. An unusual electrolyte type is the compound $(crL_3)_2\ (So_4)_3$, where L = 2-amino ethyl pyridine, for which a value of 419 $ohm^{-1}\ cm^2\ mole^{-1}$ is quoted.

# EXPERIMENTAL

## TECHNIQUES USED

All the newly synthesized compounds were characterized by their melting points, elemental analysis and conductance measurements. The site of coordination and the probable geometry of the complexes was proposed on the basis of I.R. spectroscopy.

Elemental analyses for carbon, hydrogen and nitrogen were done on a coleman analyser in the microanalytical laboratory of the Chemistry Department at Aligarh Muslim University, Aligarh, and Calcutta. The estimations of metals, sulphur and halogen were done volumetrically or gravimetrically. For the metal estimation a weighed amount of the compound was taken in silica crucible and a few drops of $H_2SO_4$ were added to decompose it. It was heated slowly till the fumes disappeared and further heating was done with concentrated nitric acid for about half an hour. The dry powder thus obtained was cooled to room temperature and was weighed as $SnO_2$. The halogen and sulphur were estimated gravimetrically by known methods.

The infrared and far infrared spectra were recorded on a Perkin Elmer621 (4000-650$cm^{-1}$) and Beckman IR 12 (650-200 $cm^{-1}$) in nujol and KBr respectively at the Instrumentation Centre of the Department of Chemistry, Aligarh Muslim University, Aligarh, and at the Department of Chemistry, Roorkee University, Roorkee.

The molar conductivity of the soluble compounds were measured in nitrobenzene or methanol on a systronics conductivity bridge type 302.

# CHAPTER III

## COMPLEXES OF ORGANOTIN(IV) HALIDES WITH DIETHYL DITHIOCARBAMATE AND PIPERAZINE(BIS)DITHIOCARBAMATE

# COMPLEXES OF ORGANOTIN(IV) HALIDES WITH DIETHYL DITHIOCARBAMATE AND PIPERAZINE (BIS)DITHIOCARBAMATE

## EXPERIMENTAL

Tributyltin chloride, trimethyltin chloride and triphenyltin acetate (All E. Merck). Sodium diethyl dithiocarbamate (B.D.H. England) m.p. 96°C was used as such. Piperazine(bis) dithiocarbamate was synthesized in the laboratory by known method[141] with a slight modification.

Preparation of piperazine bis (dithiocarbamate):

The piperazine (bis dithiocarbamate) was prepared by taking piperazine hexahydrate, carbon disulfide and sodium hydroxide in 1:2:2 molar ratio.

Piperazine hexahydrate (0.025 moles) dissolved in 100 ml isopropyl alcohol and ether mixture was kept in an ice bath at 5°C. Carbondisulphide (0.05 moles) was slowly added to this solution. Now two grams of sodium hydroxide (0.05 moles) dissolved in the minimum amount of water was added dropwise to the above mixture with continuous stirring for about four hours. Subsequently it was filtered and the filterate was kept overnight when needle shaped crystals of sodium piperazine (bis) dithiocarbamate were obtained.

## Preparation of the complexes

**Piperazine bis dithiocarbamato triphenyltin(IV)**
**$(Ph_3Sn)_2Pz(bis)dtc$:**

A solution of piperazine bis dithiocarbamate Pz(bis)dtc $Na_2$ (0.028 moles) in 20 ml ethanol was mixed in the solution of triphenyltin acetate (0.029 moles) in 15 ml ethanol. A white precipitate was immediately obtained. It was filtered, washed with the solvent and dried in vacuo.

**Piperazine bis dithiocarbamato trimethyltin(IV)**
**$(Me_3Sn)Pz(bis)dtc\ Na$:**

A solution of the ligand (0.028 moles) in 20 ml ethanol was added to trimethyltin chloride (0.028 moles) solution in 20 ml ethanol. It yielded a white crystalline compound which was filtered and dried in vacuo.

**Piperazine bis dithiocarbamato tributyltin(IV)**
**$(Bu_3Sn)Pz(bis)dtc\ Na$:**

An ethanolic solution of piperazine bis dithiocarbamate Pz(bis)dtc $Na_2$ (0.028 moles) in 20 ml ethanol was added to tributyltin chloride (0.029 moles) in 20 ml ethanol. A white powder like complex was obtained on standing the reaction mixture for a few hours. It was filtered and dried in the usual manner.

Diethyl dithiocarbamato tributyltin(IV)
$Bu_3SnEt_2dtc$:

Sodium diethyl dithiocarbamate (0.029 moles) dissolved in 20 ml of ethanol-chloroform mixture (80:20) was added to tributyltin chloride (0.029 moles) in 20 ml ethanol with continuous stirring. It gave a white powder immediately which was found to be sodium chloride on analysis. The liquid was kept overnight but did not yield any solid product. It was shaken with petroleum ether when a shining white crystalline mass was obtained.

Diethyl dithiocarbamato trimethyltin(IV)
$Me_3SnEt_2dtc$:

The ligand solution ($Et_2dtc$) (0.029 moles) in 20 ml ethanol-chloroform mixture (80:20) was slowly added to trimethyltin chloride (0.028 moles) in 15 ml ethanol with constant stirring. This mixture was further stirred for about two hours when it yielded a white solid which was filtered and dried in the usual manner.

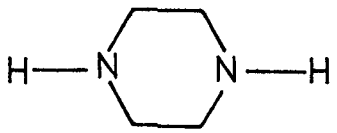
Diethyl dithiocarbamato triphenyltin(IV)
$Ph_3SnEt_2dtc$:

The diethyl dithiocarbamato (0.029 moles) dissolved in 20 ml ethanol-chloroform (80:20) mixture was added to triphenyltin acetate (0.029 moles) in 20 ml ethanol. A white powdery residue was obtained after keeping the reaction mixture for about fifteen minutes. It was filtered, washed and dried in vacuo.

## RESULTS AND DISCUSSION

All the dithiocarbamato complexes are white solids and stable at room temperature. The complexes decompose above 200°C. Since they were insoluble in the common organic solvents namely, ethanol, chloroform, nitrobenzene, nitromethane, dichloromethane, dimethyl formamide and acetonitrile, their conductance could not be measured. The analytical data along with the melting points are given in table 1. All the complexes are formed in a 1:1 metal to ligand ratio except for $(Ph_3Sn)_2Pz$ bis dtc .which has a 2:1 (M:L) ratio.

The piperazine molecule is a heterocyclic ring system having one nitrogen atom at each end of the ring.



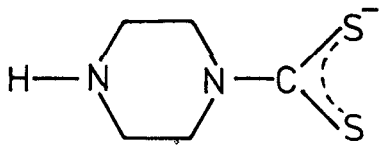
Piperazine

Two types of piperazine dithiocarbamates are known:

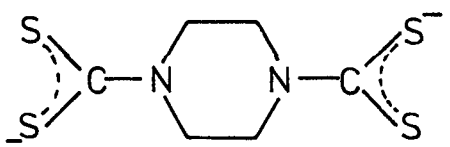
(i) Piperazine monodithiocarbamate (Pzdtc) or piperazine carbodithioate.

(ii) Piperazine bis dithiocarbamate or piperazine dicarbodithioate.

In case of mono-dithiocarbamate hydrogen atom from only one end of the piperazine molecule is replaced by a $CS_2$ group while in the bisdithiocarbamate, both the hydrogen atoms are replaced by two $CS_2$ groups.



Piperazine dithiocarbamate



Piperazine(bis) dithiocarbamate

Sodium salts of Dithiocarbamic acid are known since long. Their complexes with transition metal ions have been thoroughly investigated and mode of coordination confirmed.[142-144] However, there have been limited studies on organotin complexes having Sn-S linkage.[29] Recently organotin(IV) dithiocarbamates have been found to have potential biological activity.[145-148] These dithiocarbamate complexes are formed by a replacement reaction where the number of dithiocarbamate groups coordinated to the metal correspond to the number of anions in the organotin compound.

An attempt was made to synthesize the ligand and the dithiocarbamate complexes of a few trialkyltin (IV) halides.

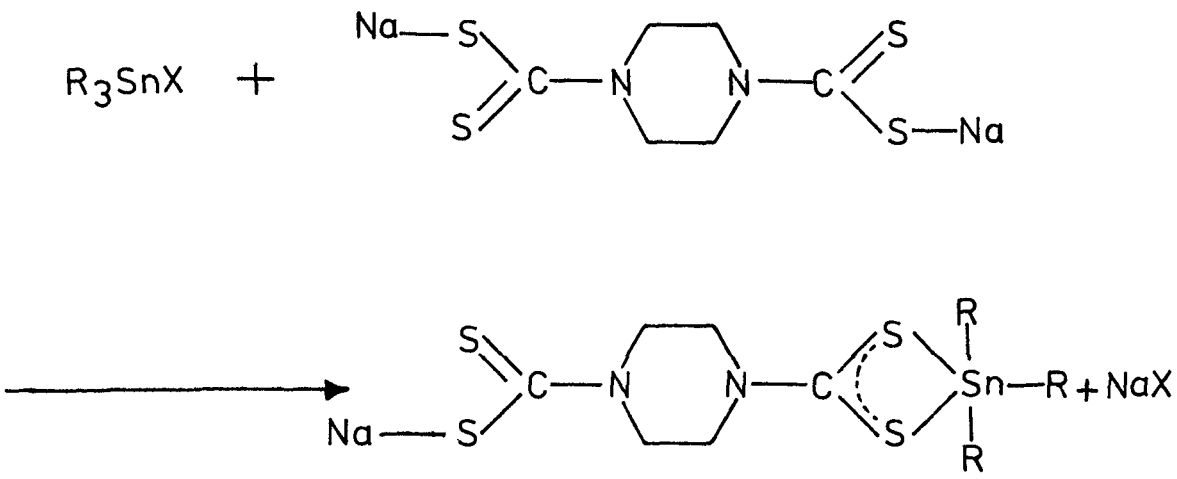
The composition of piperazine (bis) dithiocarbamate was established by elemental analysis and was further confirmed by stretching its I.R. spectrum which showed the absence of the N–H frequency indicating the removal of both hydrogen atoms from the piperazine molecule.

The triorganotin (IV) dithiocarbamates may be synthesized by any one of the following chemical reaction:

(i) By insertion of a $CS_2$ group in the presence of an amine.

$$R_3SnX + CS_2 + R_2'NH \longrightarrow R_3SnSCSNR_2' + HX$$

(ii) By a replacement reaction using the sodium salt of the dithiocarbamate.



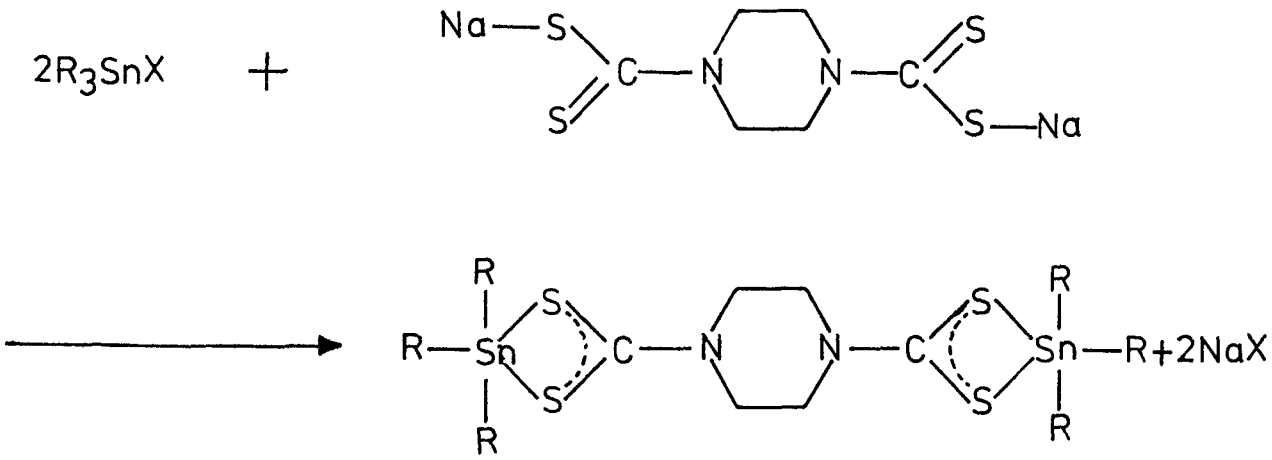
OR

Table 1

Melting Point and Analytical data of the Complexes

| Compounds | M.P. °C | % C Found (Calcd) | % H Found (calcd) | % N Found (calcd) | %Sn Found (calcd) |
|---|---|---|---|---|---|
| $(R_3Sn)_2Ps(bis)dtc.$ | 300°d | 53.68 (53.91) | 4.00 (4.06) | 3.00 (2.99) | 25.15 (25.29) |
| $R'_3SnPs(bis)dtc\ Na$ | 320°d | 25.48 (25.56) | 3.98 (4.02) | 6.60 (6.62) | 28.09 (28.03) |
| $R''_3SnPs(bis)dtc\ Na$ | 260°d | 39.47 (39.38) | 6.35 (6.38) | 5.12 (5.18) | 21.80 (21.99) |
| $R_3Snlt_2dtc$ | 200°d | 55.38 (55.48) | 5.05 (5.02) | 2.80 (2.81) | 23.68 (23.80) |
| $R'_3Snlt_2dtc.$ | 360°d | 30.94 (30.82) | 6.12 (6.10) | 4.51 (4.49) | 38.06 (38.02) |
| $R''_3Snlt_2dtc.$ | 350°d | 46.55 (46.63) | 8.48 (8.45) | 3.18 (3.20) | 27.04 (27.06) |

d = decomposition temperature, R = Phenyl, R' = Methyl, R'' = Butyl.



R = Methyl, Butyl or Phenyl
X = Chloride or Acetate

In the present case the triorganotin (IV) dithiocarbamates have been synthesized by the second method shown above. In all the cases, efforts were made to synthesize 2:1 complexes, however, except for triphenyltin piperazine (bis) dithiocarbamate ($Ph_3Sn_2Pzbis(dtc)$ all other complexes were formed in a 1:1 metal to ligand ratio, irrespective of the quantities of the reactants used.

The dithiocarbamates have been found to be of particular interest from the structural point of view owing to the fact that they can act both as chelates or monodentate ligands.[20,21] For all dithiocarbamate complexes a partial double bond character for the  group has been confirmed by I.R. spectral studies.[24,25] It has been further established that for a symmetrically coordinated dithiocarbamate moiety there is only one C-S band around 1000 $cm^{-1}$, whereas the presence of two

closely spaced bands in the same region indicate an unsymmetrically bond dithiocarbamate group.[22,23,149,150]

The infrared spectra of the ligands and complexes have been studied in the region 4000-200 $cm^{-1}$. The important frequencies helpful in the structure elucidation of the newly synthesised compounds have been given in table 2. The C-S stretching frequencies in the I.R. spectra of dithiocarbamate complexes are very diagnostic in distinguishing. The symmetrically or unsymmetrically bound C-S group to a metal ion. It is a well established fact that a doublet in 1000 $\pm$ 50 $cm^{-1}$ region indicates presence of an unsymmetrically bound dialkyl dithiocarbamate,[25] whereas for an unsymmetrical heterocyclic derivative a doublet appears over a wider range 1000 $\pm$ 70 $cm^{-1}$.[141] However, for all types of symmetrically bound dithiocarbamato group a single band is observed at around 1000 $cm^{-1}$.[141] A strong band at 1510 $cm^{-1}$ region of the spectrum is attributed to the (C=N) stretching mode. There is no absorption band in the far I.R. region of the free ligand.

The I.R. spectra of the newly synthesised organotin (IV) dithiocarbamates have been found to be almost unchanged in the range quoted above as compared with that of the free ligand, except for the absorption around 1500 $cm^{-1}$ region assigned to $S_2CN$ stretching frequency.

Piperazine bis(dithiocarbamate) and diethyl dithiocarbamate complexes show only one C-S absorption band at 1000 $cm^{-1}$ which is diagnostic of symmetrical coordination of the dithiocarbamate

Table 2

I.R. Spectra of the complexes and their assignment

| Compounds | $\nu$(C—N) | $\nu$(C—S) | $\nu$(M—S) |
|---|---|---|---|
| $Na_2Pabis(dtc)_2$ | 1450 VS | 1000 S | - |
| $R_3SnPz(bis)dtc.$ | 1460 S | 1000 VS | 370 m |
| $R'_3SnPz(bis)dtcNa$ | 1485 S | 1000 VS | 400 Vw |
| $R''_3SnPz(bis)dtcNa$ | 1460 S | 1000 VS | 390 S |
| $NaEt_2dtc$ | 1500 VS | 1000 VS | - |
| $R_3SnEt_2dtc.$ | 1510 S | 1000 S | 398 m |
| $R'_3SnEt_2dtc.$ | 1535 S | 998 VS | 390 W |
| $R''_3SnEt_2dtc.$ | 1515 S | 990 b | - |

R = Phenyl
R' = Methyl
R" = Butyl
VS = Very strong
S = Strong
m = medium
b = broad
W = weak
vw = very weak

moiety. A strong band at around 1455 $cm^{-1}$ in all the cases has been assigned to the C=N stretching mode. The $\nu$ (C=N) in the piperazine bis(dithiocarbamate) appears at a slightly lower frequency as compared to that of dialkyl dithiocarbamate. This may be due to the fact that piperazine has rigid heterocyclic ring system which minimizes the release of electrons towards carbon and nitrogen bond as a consequence of which the carbon nitrogen bond has a lesser double bond character.

The piperazine bis dithiocarbamate can act both as a bidenate or a quadridentate ligand coordinating through one or both dithiocarbamate units in the present case. All the complexes formed have a 1:1 metal to ligand ratio except for $(Ph_3Sn)_2Pz(bis)dtc$, which is formed in a 2:1 (M:L) ratio, where both the $NCS_2$ groups are coordinated to two tin atoms at both the ends of the piperazine ring.

The far I.R. region (650-200 $cm^{-1}$) is very important for the structure elucidation of the metal complexes. The metal halogen (M-X) and metal ligand (M-L) stretching frequencies appeared in this region. Since there is a single anion in the triorganotin (IV) halides which is replaced by $S_2CN$ group, there is obviously to M-X absorption band in the far I.R. region of the complexes. However, new peaks observed at around 400 $cm^{-1}$ region (Table 2) (which are absent in the free ligands) are assigned to the M-S stretching frequencies.[151,152]

On the basis of above studies a penta coordinated tin atom with trigonal bipyramidal geometry may be proposed for these organotin (IV) dithiocarbamate.

# CHAPTER IV

## ADDITION COMPOUNDS OF TRIALKYLTIN(IV) HALIDES WITH PIPERAZINE, ACRIDINE, PYRROLIDINE, 1,10-PHENANTHROLINE AND 2,2'-BIPYRIDYL

# ADDITION COMPOUNDS OF TRIALKYLTIN (IV) HALIDES WITH PIPERAZINE, ACRIDINE, PYRROLIDINE, 1,10-PHENANTHROLINE AND 2,2'-BIPYRIDYL

## EXPERIMENTAL

Triphenyltin chloride (TPT), tributyltin chloride (TBT), trimethyltin chloride (TMT), piperazine hexahydrate (E. Merck), acridine, pyrrolidine, 1,-10-phenanthroline and 2,2'-bipyridyl (B.D.H.) were used without further purification. The solvents, ethanol, methanol and nitrobenzene were distilled and dried by conventional methods.

### Preparation of piperazine adducts

### (TPT). Piperazine

Piperazine (0.0038 moles) dissolved in 20 ml alcohol was added to a solution of triphenyltin chloride (0.0039 moles) in 15 ml alcohol. After keeping this mixture in an ice bath for about twentyfour hours a white shining crystalline mass was obtained. It was recrystallised from methanol (yield 60 %).

### (TBT). Piperazine and (TMT). Piperazine

Piperazine (0.0038 moles) dissolved in 20 ml alcohol was added to a solution of tribytyltin chloride (0.0038 moles) in 10 ml alcohol. A similar amount of the ligand was added to a solution

of trimethyltin chloride (0.0038 moles) in 10 ml ethanol. These reaction mixtures were cooled to 2°C, when TBT and TMT yielded off white and white solids, respectively. These were recrystallised from methanol and dried in vacuo (yields 60 % and 65 %, respectively).

Preparation of acridine adducts

The ligand solution (0.0037 moles) dissolved in 15 ml ethanol was mixed with triphenyltin chloride solution (0.0039 moles) in 15 ml ethanol (I). The same amount of the ligand dissolved in ethanol was separately added to tributyltin chloride (II) (0.0037 moles) and trimethyltin chloride (III) (0.0038 moles) in 10 ml ethanol. The reaction mixtures were stirred for about three hours and kept in an ice bath. They yielded light brown and yellowish solid complexes which were filtered and dried in the usual manner (yields I 65 %, II 55 % and III 50 %).

Preparation of pyrrolidine adducts

(TPT). Pyrrolidine

Triphenyltin chloride (0.0038 moles) in 15 ml ethanol was mixed with pyrrolidine (0.038 moles) in 10 ml ethanol which immediately resulted in the formation of a buff precipitate. It was filtered and dried in vacuo (yield 80 %).

(TBT). Pyrrolidine

Pyrrolidine (0.0108 moles) in 10 ml ethanol was added to tributyltin chloride solution (0.0108 moles) in 15 ml ethanol. This mixture yielded a pale yellow sticky compound, on keeping in an ice bath for a few hours. It was filtered and dried in vacuo (yield 65 %).

Preparation of the phenanthroline adducts

(TPT). Phenanthroline

A solution of triphenyltin chloride (0.0038 moles) in 15 ml ethanol was added to phenanthroline solution (0.038 moles) in 20 ml ethanol. The volume of this mixture was reduced to half by evaporating it on a water bath. It gave white needle shaped crystals on standing overnight at 5°C (yield 75 %).

(TBT). Phenanthroline

Phenanthroline dissolved (0.038 moles) in 20 ml ethanol was added to tributyltin chloride (0.0038 moles)in 10 ml ethanol. This mixture yielded a pink solid on standing for three hours. It was filtered and dried under vacuum (Yield 70 %).

Preparation of the 2,2'-Bipyridyl adducts

(TPT). Bipyridyl and (TBT). Bipyridyl

2,2'-bipyridyl (0.0038 moles) dissolved in 15 ml ethanol was added to a solution of triphenyltin chloride (0.0038 moles) in 20 ml ethanol and the same amount of bipyridyl was added to

tributyltin chloride (0.0038 moles) in 15 ml ethanol. After a few hours TPT and TBT adducts of bipyridyl were obtained as white granular solid and white needle shaped crystals, respectively They were filtered off and dried in the usual manner (yields, 70 % and 75 %).

## RESULTS AND DISCUSSION

All the newly synthesized addition compounds are stable to air and moisture except for the tributyltin chloride adduct of pyrrolidine which is viscous and decomposes on exposure to air. The composition of the adducts was established by elemental analysis. The melting points and analytical data of the adducts are given in table 3. The infrared spectra were run in nujol in the range 4000-200 $cm.^{-1}$ The characteristic frequencies required for the structure elucidation of these adducts and their assignments are given in table 4. All these compounds are soluble in nitrobenzene except for the piperazine adducts which dissolve only in methanol. All the adducts are formed in a 1:1 (M:L) ratio.

Trialkyltin (IV) chloride form two types of adducts with monodentate ligands, (1) $R_3SnX.L$ and (2) $R_3SnX.L'_2$ where L is the ligand. When the complex is formed with a bidentate ligand, L', it may achieve a trigonal bipyramidal structure or it may have an octahedral geometry.[153-154] The stereochemistry of the adducts of tin (IV) halides depends mainly on the size and donor properties of the ligands. It is found that smaller ligands are more likely to form $R_3SnX_2$ type complexes with the two ligands cis to each other, while larger or bidentate ligands form either a 1:1 or a 1:2 addition compounds where the ligands are essentially trans to each other for steric reasons.

Tin (IV) halides are well known Lewis acids and they interact

Table 3

Melting points, analytical data and molar conductance of Trialkyltin(IV) halide adducts

| Adducts | M.P. °C | % C Found (Calcd) | % H Found (Calcd) | % N Found (Calcd) | %Cl Found (Calcd) | %Sn Found (Calcd) | Molar Conductance* $ohm^{-1}cm^2mole^{-1}$ |
|---|---|---|---|---|---|---|---|
| TMT (Ps) | 180 | 30.10 (29.46) | 6.62 (6.66) | 9.75 (9.82) | 12.14 (12.45) | 41.34 (41.59) | 0.003 |
| TPT (Ps) | 94 | 55.81 (56.03) | 5.27 (5.30) | 5.79 (5.94) | 7.35 (7.53) | 25.50 (25.17) | 0.235 |
| TBT (Ps) | 145-47 | 47.16 (46.70) | 8.79 (9.00) | 6.93 (6.81) | 8.71 (8.63) | 28.60 (28.84) | 0.289 |
| TMT (Adc.) | 115 | 50.81 (50.78) | 4.78 (4.76) | 3.65 (3.70) | 9.58 (9.38) | 31.41 (31.56) | 0.000 |
| TPT (Adc.) | 132 | 66.13 (65.94) | 4.20 (4.25) | 2.40 (2.49) | 6.10 (6.29) | 21.36 (21.02) | 0.005 |
| TBT (Adc.) | 80 | 60.81 (59.50) | 7.27 (7.14) | 2.85 (2.77) | 7.29 (7.04) | 23.55 (23.52) | 0.000 |
| TPT (Pycr.) | 130 | 56.90 (57.88) | 5.44 (5.26) | 2.86 (3.06) | 8.03 (7.78) | 25.75 (26.00) | 0.642 |
| TBT (pycr.) | 160 | 48.85 (48.47) | 9.30 (9.08) | 3.72 (3.53) | 9.20 (8.96) | 30.01 (29.94 | 0.000 |
| TPT (Phen.) | 145 | 63.48 (63.70) | 3.86 (4.07) | 4.56 (4.95) | 6.20 (6.28) | 20.78 (20.99) | 0.000 |
| TBT (Phen.) | 200 | 56.89 (57.02) | 6.94 (6.93) | 5.49 (5.54) | 7.07 (7.03) | 23.69 (23.48) | 0.001 |
| TPT (2,2'-Bipy.) | 148 | 61.82 (62.09) | 4.19 (4.25) | 4.87 (5.17) | 6.34 (6.56) | 21.43 (21.90) | 0.000 |
| TBT (2,2'-Bipy.) | 162 | 54.82 (54.87) | 7.51 (7.27) | 5.79 (5.61) | 6.98 (7.37) | 24.44 (24.65) | 0.000 |

* Molar conductance of $10^{-3}$ M solutions.

Table 4

I.R. Spectra of Trialkyltin(IV) halide adducts and their assignments

| Adducts | $\nu$(N-H) | $\nu$(C-N) | $\nu$(C=N) and $\nu$(C=C) | $\nu$(Sn-N) | $\nu$(Sn-X) |
|---|---|---|---|---|---|
| Piperazine | 3328 b | 1444 s | - | - | - |
| TME (Pz) | 2985 m | 1495 s | - | 300 w | 365 |
| TPT (Pz.) | 3040 b | 1475 m | - | 300 w | 355 |
| TBT (Pz.) | 3040 | 1478 s | - | 300 w | 355 |
| Aziridine | - | - | 1555 s, 1515 s | - | - |
| TMT (Azr.) | - | - | 1618 s, 1650 w | 300 | 355 |
| TPT (Azr.) | - | - | 1635 w, 1520 | 300 | 385 |
| TBT (Azr.) | - | - | 1630 w, 1545 sh | 300 | 390 |
| Pyrrolidine | 3268 b | - | - | - | - |
| TPT (Pyrr.) | 3060 b | - | - | 310 | 330 |
| TBT (pyrr.) | 2900 | - | - | 300 | 370 |
| O-phenanthroline | - | - | 1499, 1415 | - | - |
| TPT (Phen.) | - | - | 1520, 1465 | 300 | 390 |
| TBT (Phen.) | - | - | 1584, 1495 | 300 | 340 |
| 2,2'-Bipyridyl | - | 1500, 1400 | - | - | - |
| TPT (2,2'-Bipy) | - | 1580, 1475 | - | 300 | 370 |
| TBT (2,2'-Bipy.) | - | 1580, 1464 | - | 300 | 415 |

with various Lewis bases to form donor acceptor type complexes.[155] Similar addition compounds of the corresponding alkyl halides with various nitrogen bases have been studied with a view to examine their influence on the stereochemistry of the adducts.

Piperazine adducts

The infrared spectrum of piperazine shows absorptions at 3328 $cm^{-1}$ and 1444 $cm^{-1}$ attributed to N-H and C-N stretching frequencies respectively. There is an electronic drift from nitrogen atom towards tin atom after coordination, which necessarily weakens the N-H bond with a consequent decrease in N-H stretching frequencies in the complexed piperazine.[156]

The C-N absorption modes appeared at 1475 $cm^{-1}$, 1478 $cm^{-1}$ and 1565 $cm^{-1}$ in triphenyltin chloride, tributyltin chloride and trimethyltin chloride adducts respectively. In case of trimethyltin chloride adduct the $\nu$(N-H) is observed at 2985 $cm^{-1}$ while in both tributyltin chloride and triphenyltin chloride adducts it has been observed at 3040 $cm^{-1}$. These adducts show M-N stretching frequency at around 300 $cm^{-1}$. There is only one M-Cl stretch in these adducts at 365 $cm^{-1}$, 355 $cm^{-1}$ and 355 $cm^{-1}$.

Acridine adducts

Acridine shows two absorption bands at 1515 $cm^{-1}$ and 1555 $cm^{-1}$ in its I.R. spectrum which are assigned to C=N and C=C stretching frequencies. It is difficult to distinguish between the C=C and C=N absorption bands because they appear in the same region

of the spectrum. It is known that the coordination of tin atom through hetero-nitrogen atom of the ligand caused an increase in its C=N stretching frequency which is evident by a marked increase in $\nu$ (CN) observed in these cases. These shifts are in consonance with those reported for adducts with similar donor molecules.[157,158]

The I.R.spectra of triphenyltin chloride (TPT) tributyltin chloride (TBT) and trimethyltin chloride (TMT) adducts show an increase of 63-85 $cm^{-1}$ in C=N stretching frequencies. The M-Cl absorption bands in the far I.R. region of the spectrum are stronger and found at a higher wave number as compared to M-N absorption bands. A weak band noted at around 300 $cm^{-1}$ in all the adducts has been assigned to $\nu$ (M-N).[159] The M-Cl stretching frequencies in triphenyltin chloride (TPT), tributyltin chloride (TBT) and trimethyltin chloride (TMT), have been observed at 390, 385 and 355 $cm^{-1}$ respectively.

Pyrrolidine adducts

The $\nu$ (N-H) in pyrrolidine appears at 3368 $cm^{-1}$. The coordination of metal through nitrogen causes a decrease in the N-H bond strength with a consequent decrease in N-H stretching frequencies. In case of TPT and TBT adducts, the $\nu$ (N-H) has been found to be shifted to lower wave numbers at 3060 $cm^{-1}$ and 2900 $cm^{-1}$ respectively. The TPT adduct shows $\nu$(M-N) at 310 $cm^{-1}$ and $\nu$(M-Cl) at 330 $cm^{-1}$. The $\nu$(M-N) and $\nu$(M-Cl) peaks in the TBT adducts are observed at 300 $cm^{-1}$ and 370 $cm^{-1}$ respectively.

Phenanthroline adducts

The I.R. spectrum of phenanthroline undergoes slight modification on coordination to a metal ion. Particularly the region from 1600 to 1400 $cm^{-1}$ where the C=C and C=N stretching frequencies occur, undergoes small shifts to higher wave numbers.[160] The bands at 1499 $cm^{-1}$ and 1415 $cm^{-1}$ in the free ligand are shifted to higher wave numbers at 1520 $cm^{-1}$ and 1465 $cm^{-1}$ in the triphenyltin chloride adduct and at 1584 $cm^{-1}$ and 1495 $cm^{-1}$ in tributyltin chloride adduct.

A new absorption band occurs at about 1150 $cm^{-1}$ (Band I) in the adducts of phenanthroline, if it is chelated. The weak absorption band at 1131 $cm^{-1}$ is shifted towards lower frequencies in addition to a medium strong band at 876 $cm^{-1}$ in the complexes whereas it appears as a shoulder in the free ligand.[160] Another band at 620 $cm^{-1}$ (Band II) also shifts towards higher frequency region on chelation.

We have observed the band I at 1150 $cm^{-1}$ in triphenyltin chloride and at 1139 $cm^{-1}$ in tributyltin chloride. The band II has been observed at 638 $cm^{-1}$ in both these complexes.

The $\nu$ (M-N) in these adducts found around 300 $cm^{-1}$. The $\nu$(M-Cl) is observed at 350 and 340 $cm^{-1}$ respectively.

2,2'-Bipyridyl adducts

The infrared spectrum of 2,2'-bipyridyl is nearly similar to that of 1,10-phenanthroline because of the similar position of

nitrogen atoms in both these molecules. The C-C and C-N stretching frequencies have been observed at 1580 $cm^{-1}$ and 1475 $cm^{-1}$. The bands which have been suggested to be most diagnostic of coordination[161] of bipyridyl to a metal ion are those at 995 $cm^{-1}$ and 759 $cm^{-1}$ in the free ligand.[160,161] It has been suggested that the out of plane (CH) vibrations occur at 750 $cm^{-1}$ in the bipyridyl derivatives. In the case of TPT and TBT adducts the former band has been found to be shifted to 1018 $cm^{-1}$ and 1033 $cm^{-1}$ respectively. The latter band has been found to absorb at 760 $cm^{-1}$ in both the adducts with an increase in intensity.

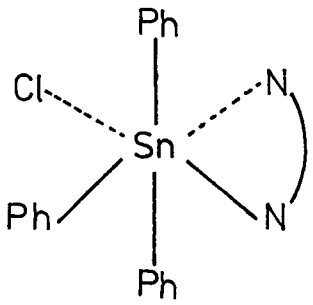
The far I.R. region of the TPT adduct showed $\nu$(M-N) at 300 $cm^{-1}$ and $\nu$(M-Cl) at 370 $cm^{-1}$ while in the case of TBT adduct the $\nu$(M-N) and $\nu$(M-Cl) have been observed at 300 $cm^{-1}$ and 415 $cm^{-1}$ respectively.

In addition to $\nu$(Sn-N) and $\nu$(Sn-Cl), the $\nu$(Sn-C) is also helpful in determining the configuration of $SnC_3$ and $SnC_2$ moieties in $R_3SnX$ and $R_2SnX_2$ derivatives. It is known that if the spectrum in the region 580-500 $cm^{-1}$ exhibits two Sn-C stretching modes symmetric and asymmetric, the configuration of $SnC_3$ group is non-planar or that of $SnC_2$ group is non-linear. However, if there is only one band assigned to $\nu$(Sn-C) in the above region, the $SnC_3$ group is planar or $SnC_2$ group is linear.[126] This criterion has been further supported by X-ray diffraction studies. In the present case all the addition compounds revealed only one Sn-C band in the region 580-500 $cm^{-1}$ which

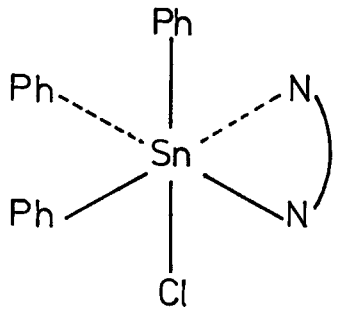
confirms that the configuration of $SnC_3$ group in triorganotin compounds is planar.

On the basis of above studies, it has been concluded that the addition compounds of acridine, piperazine and pyrrolidine may have a trigonal bipyramidal geometry,(with the planar arrangement of alkyl groups) which is the most stable configuration for the pentacoordinated tin atom. These results are in consistency with the geometries of tin compounds reported earlier.[162]

For an octahedral compound with bidentate ligands like 1,10-phenanthroline and 2,2'-bipyridyl, two types of configurations are possible.[163]




(A) Meridional Isomer




(B) Facial Isomer

Configuration B is ruled out on the basis of only one Sn-C band and also on the assumption that the alkyl groups (in the present case butyl and phenyl groups) will not occupy a position cis to each other, because the molecule will be sterically hindered and such a strained situation will lead to the destabilization of the octahedral configuration. An octahedral structure of the type (A) may therefore, be proposed for the phenanthroline and bipyridyl adducts although their symmetry will be lowered.

# CHAPTER V

## COMPLEXES OF ORGANOTIN (IV) HALIDES WITH ANTIPYRINE, 4-AMINOANTIPYRINE, BENZO(c)-, BENZO(f)- AND BENZO(h) QUINOLINES

# COMPLEXES OF ORGANOTIN (IV) HALIDES WITH ANTIPYRINE, 4-AMINO ANTIPYRINE, BENZO(e)-, BENZO (f)- AND BENZO (h) QUINOLINES

## EXPERIMENTAL

Trialkyltin (IV) chlorides and dibutyltin di-acetate were obtained from E. Merck. Antipyrine (apy), 4-aminoantipyrine (aapy.), benzo (e) quinoline (beq), benzo (f) quinoline (bfq) and benzo (h) quinoline (bhq) (Fluka, A.G.) were used without further purification. Solvents used were distilled and dried by conventional methods.

The infrared spectra (4000-600 $cm^{-1}$) were recorded in KBr and the far infrared (650-200 $cm^{-1}$) in nujol on a Perkin Elmer spectrophotometer. Conductivity measurements of $10^{-3}$M solutions in nitrobenzene were made on a systronics conductivity bridge type 302.

### Preparation of the Complexes

Organotin (IV) halides and quinolines dissolved in alcohol chloroform mixture were mixed together in equimolar quantities. These mixtures were stirred thoroughly and kept at 5°C for about two days when they yielded solid products. They were washed, filtered and dried under vacuum.

## RESULTS AND DISCUSSION

The analytical data (Table 5) indicate that all the complexes of trialkyltin (IV) halides and dialkyltin (IV) dihalide with antipyrine, 4-amino antipyrine, benzo (c) quinoline, benzo (f) quinoline and benzo (h) quinoline have a 1:1 metal to ligand ratio except for those of triphenyltin chloride and tributyltin chloride complexes of benzo (c) quinoline which are of the type $R_3SnX.L_2$. These complexes are fairly stable to oxidation by air and moisture at room temperature. The molar conductance of $10^{-3}$M solutions in nitrobenzene exhibit their non-ionic behaviour.

The antipyrine molecule has two coordination sites, namely oxygen and nitrogen atoms in the ring.[35,36] It has a negative potential at the oxygen end of the carbonyl group which is susceptible to coordination. The unidentate behaviour of antipyrine has been shown earlier, although the involvement of ring nitrogen atom is also conceivable but is unlikely.[39] In a large number of antipyrine adducts, the ligand has been shown to be unidentate coordinating through the oxygen atom only.[39,164,165] All the assignments have been made with the assumption that antipyrine has a mono-substituted benzene, the substituent being a five membered ring.[40]

The I.R. spectrum of antipyrine showed an intense band at 1666 $cm^{-1}$ which is attributed to the C=O stretching frequency. This band in the complexed antipyrine has been observed at a

Table 5

Analytical data of the complexes

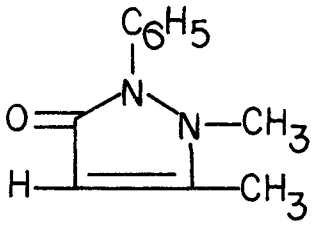
| Compound | MP °C | % C Found (calcd.) | % H Found (calcd.) | % N Found (calcd.) | % Cl Found (calcd.) | % Sn Found (calcd.) | Molar conductance* $Ohm^{-1}$ $Cm^2$ $moles^{-1}$ |
|---|---|---|---|---|---|---|---|
| TNT (AApy) | 135 | 41.59 (41.78) | 5.46 (5.47) | 10.49 (10.44) | 8.69 (8.82) | 29.46 (29.49) | 0.0017 |
| TPT(AApy) | 90 | 59.15 (59.17) | 4.77 (4.76) | 7.18 (7.14) | 6.08 (6.03) | 20.14 (20.16) | 0.0034 |
| DBTA(AApy) | 80 | 49.88 (49.85) | 6.68 (6.68) | 7.53 (7.58) | - - | 21.44 (21.42) | 0.0002 |
| T4T (Apy) | 132 | 44.48 (44.43) | 5.44 (5.42) | 7.27 (7.23) | 9.15 (9.17) | 30.81 (30.60) | 0.0002 |
| TPT(Apy) | 130 | 60.77 (60.72) | 4.73 (4.71) | 4.85 (4.86) | 6.18 (6.19) | 20.66 (20.69) | 0.0025 |
| DBTA(Apy) | 125 | 51.29 (51.24) | 6.64 (6.68) | 5.17 (5.19) | - - | 22.00 (22.02) | 0.0024 |
| TBT(BCq)$_2$ | 107 | 66.77 (66.75) | 6.53 (6.58) | 4.06 (4.09) | 5.14 (5.19) | 17.33 (17.36) | 0.0008 |
| TPT(BCq)$_2$ | 97-100 | 71.02 (71.05) | 4.42 (4.44) | 3.79 (3.76) | 4.79 (4.77) | 15.89 (15.96) | 0.0014 |
| T4T(BCq) | 180 | 50.73 (50.78) | 4.75 (4.76) | 3.72 (3.70) | 9.33 (9.38) | 31.32 (31.36) | 0.0010 |

(Contd.)

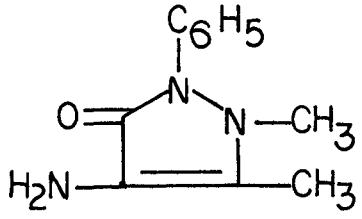
Table 5 (Contd.)

| Compound | MP °C | % C Found (Calcd.) | % H Found (Calcd.) | % N Found (Calcd.) | % Cl Found (Calcd.) | % Sn Found (Calcd.) | Molar conductance* $Ohm^{-1}$ $cm^2$ $moles^{-1}$ |
|---|---|---|---|---|---|---|---|
| DBTA(BCq) | 130 | 56.61 (56.64) | 6.22 (6.23) | 2.63 (2.64) | - | 22.38 (22.39) | 0.0003 |
| TBT(Béq) | 50 | 59.50 (59.51) | 7.11 (7.14) | 2.78 (2.77) | 7.01 (7.04) | 23.51 (23.52) | 0.0016 |
| TPT(Béq) | 118 | 65.90 (65.94) | 4.28 (4.25) | 2.40 (2.48) | 6.28 (6.29) | 21.00 (21.02) | 0.0004 |
| TMT (Béq) | 110 | 50.74 (50.78) | 4.71 (4.76) | 3.75 (3.70) | 9.39 (9.38) | 31.38 (31.36) | 0.0004 |
| DBTA(Béq) | 95-100 | 56.66 (56.64) | 6.26 (6.23) | 2.63 (2.64) | - | 22.34 (22.39) | 0.0011 |
| TPT(Bhq) | 110 | 65.99 (65.94) | 4.25 (4.25) | 2.44 (2.48) | 6.25 (6.29) | 21.03 (21.02) | 0.0017 |
| DBTA(Bhq) | 100 | 56.61 (56.64) | 6.22 (6.23) | 2.66 (2.64) | - | 22.35 (22.39) | 0.0022 |
| $SnCl_2(Bhq)_2$ | 233 | 57.15 (57.18) | 2.91 (2.93) | 5.10 (5.13) | 13.00 (13.01) | 21.73 (21.73) | 0.0027 |

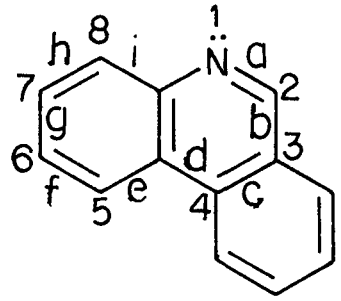
* Molar conductance of $10^{-3}$ M solutions.



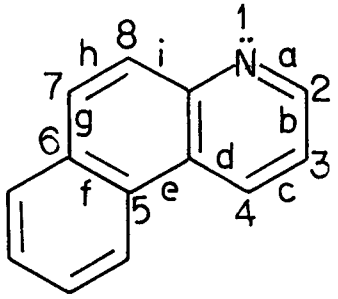

Antipyrine



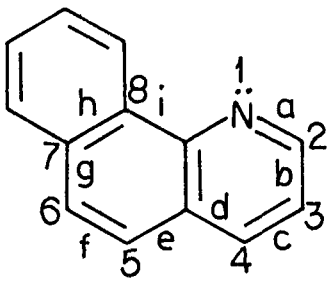

4-Amino antipyrine




Benzo(c) quinoline




Benzo(f) quinoline




Benzo(h) quinoline

lower frequency in all the cases indicating coordination of tin through oxygen atom of the carbonyl group. The strong bands at 1582 and 1505 $cm^{-1}$ are assigned to the ring stretching of pyrazolone in antipyrine. Five membered heteroaromatic compounds are found to give two strong bands at approximately 1590 $cm^{-1}$ and 1490 $cm^{-1}$ which are considered to be characteristic of five membered ring.[166,167] The bands assigned to the vibrations of the benzene ring compare well with those of mono-substituted derivatives of benzene.[168] The ring stretching vibrations result probably due to the complete interaction of $\nu$(C=N) vibrations (Table 6 ) and it is therefore difficult to distinguish different vibrations. The ring stretching frequencies in complexes of antipyrine and its derivatives are observed in 1500-1620 $cm^{-1}$ region.

The 4-amino antipyrine molecule may coordinate through carbonyl oxygen or amino nitrogen or through both.[37,38] After complexation a shift in $\nu$(C=O) to lower wave number is indicative of coordination through carbonyl oxygen.[39] A lowering of $\nu$(N-H) in 4-amino antipyrine is also due to the hydrogen bonding through the halogen of the metal halide but in the case of $R_3SnX$ the coordination of nitrogen would probably be preferred over hydrogen bonding because it would lead to a distorted octahedral geometry.

I.R. spectra of quinoline complexes

The assignment of I.R. spectra of benzo (c)-, benzo (f)-,

benzo (h) quinolines and their complexes have been presented in table 6. Characteristic ring vibrations appear in the range 1600-1350 $cm^{-1}$ in most of the heterocyclic compounds.[74] The ring stretching vibrations probably result from the complete interaction of $\nu$(C=C) and $\nu$(C=N) vibrations, since these vibrations appear in the same region of the spectrum it is difficult to identify them separately.

The coordination of the metal through the ring nitrogen atom causes an increase in the C=C and C=N stretching frequencies in the above donor molecules similarly as in the complexes of pyridine, quinoline and pyrimidine.[74,169,170] The C=C and C=N stretching bands in quinolines normally appear in 1640 to 1500 $cm^{-1}$ region which have been found to be increased after complexation. In the case of Benzo (e) quinoline strong bands at 1615 $cm^{-1}$, 1570 $cm^{-1}$ and 1520 $cm^{-1}$ have been noted. These bands show a little increase in frequency in all the complexes.

In the case of benzo (f) quinoline complexes the $\nu$(C=C) and $\nu$(C=N) frequencies did not seem to be very sensitive to coordination because these bands have not shown substantial increase. It seems reasonable because the drain of electrons towards the nitrogen atom in benzo (f) quinoline will be less than in benzo (e) quinoline. This difference is due to the change in the position of aromatic ring. These frequencies are also not much different in benzo (h) quinoline complexes.

The formation of a metal-carbon sigma bond in benzo (h) quinoline may be envisaged if the ligand fulfills the following

Table 6

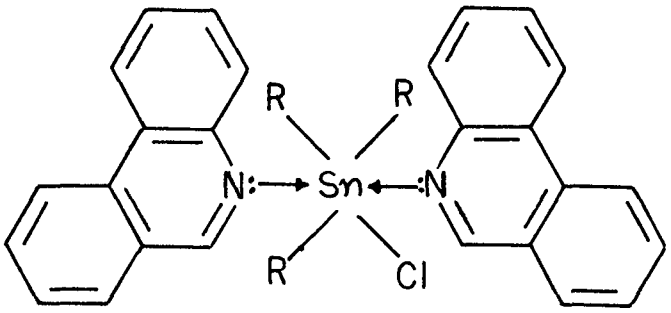
I.R. Spectra of ligands, complexes and their assignments.

| Complex | ν(N-H) | ν(C=O) | ν(C=C) ν(C=N) | ν(M-N) | ν(M-O) | ν(M-X) |
|---|---|---|---|---|---|---|
| Aapy | 3435 m<br>3330 m | 1650 vs<br>1600 m | - | - | - | - |
| AMT(Aapy.) | 2900 w<br>2840 w | 1620 w | - | 540 | 520 | 460 |
| TPT(Aapy.) | 2850<br>3020 m | 1600 w<br>1580 m | - | 475 m | 440 vs | 390 s |
| EDTA(Aapy.) | 3160 w<br>2900 b,m | 1570 | - | 565 | 470 | 390 |
| Apy | - | 1665 vs | - | - | - | - |
| TNT(Apy) | - | 1600<br>1550 | - | 500 | 470 | 380 |
| TPT (Apy.) | - | 1580<br>1560 | - | 590 | 535 w | 430 w |
| EDTA (Apy.) | - | 1580 | - | - | - | - |
| BCq | - | - | 1615<br>1570 s<br>1520 m | - | - | - |
| TBT$(BCq)_2$ | - | - | 1620 w<br>1590 w<br>1580 w | 500 | - | 470 |
| TPT $(BCq)_2$ | - | - | 1650 w<br>1620 w<br>1530 w | 440 vs | - | 380 s |

(Contd.)

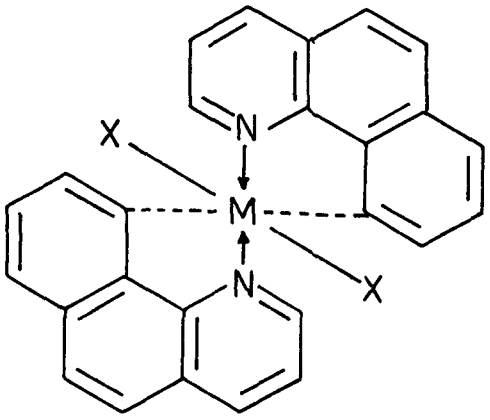
Table 6 (Contd.)

| Complex | ν (N-H) | ν(C=O) | ν(C=C) ν(C=N) | ν(M-N) | ν(M-O) | ν (M-X) |
|---|---|---|---|---|---|---|
| TAT (BCq) | - | - | 1615 vs<br>1590 s<br>1575 s | 450 s | - | 395 s |
| DBTA(BCq) | - | - | 1620 w<br>1600 w<br>1580 w | 590 w | - | 475 |
| (BBq) | - | - | 1600<br>1580 | - | - | - |
| TBT(BBq) | - | - | 1600 sh<br>1560 s<br>1490 s | 525 s | - | 465 w |
| TPT (BBq) | - | - | 1590 | - | - | - |
| TAT (BBq) | - | - | 1600 w<br>1580 w | 490 vs | - | 350 s |
| DBTA(BBq) | - | - | 1600 s<br>1490 | 560 | - | 410 |
| (Bbq) | - | - | 1605 s<br>1575 s<br>1552 m | - | - | - |
| TPT (Bbq) | - | - | 1580 w | 560 | - | 460 |
| DBTA(Bbq) | - | - | 1600 b | 520 | - | 390 |




$R_3SnCl(Bcq)_2$

R = Ph or Bu




$SnCl_2(Bhq)_2$

requirements:[45]

i) Nitrogen is tertiary,

ii) There exists a possibility of the formation of a five membered ring containing the metal, and

iii) A hydrogen ion attached to the aromatic carbon is displaced by the metal ion.

It is important to note that the tertiary nitrogen atom in benzo(h) quinoline occupies a position such that it may form a five membered ring if the carbon atom is metallated. Reports have appeared wherein several substituted quinolines and similar other donor molecules have been shown to form simultaneously the M-N and the M-C $\sigma$ bond.[45,46,171,172] Unlike with those of transition metal ions, the reaction of trialkyltin halide and dialkyltin dihalide with benzo (h) quinoline did not evolve any HCl, suggesting the lack of the formation of a M-C sigma bond. Besides these a comparison of the H'N'R spectra of both the ligand and complexes in $CCl_4$ did not show the replacement of a proton from position ten in the ring.

It seems appropriate to examine the possibility of the occurrence of the above reaction of benzo (h) quinoline with tin (IV) chloride in which the absence of the bulky organic groups attached to the tin atom, makes it sterically considerably more facile. Indeed this expectation was more than fulfilled in the formation of two metal-carbon sigma bonds in the 1:2 octahedral compound.

The far I.R. region of pyrazolone and quinoline complexes of $R_3SnX$ and $R_2SnX_2$ show new but weak bands in the region below

600 $cm^{-1}$. In the far I.R. spectra of pyrazolone complexes, the M-N, M-O and M-X frequencies have been identified,[173-176] (Table 6 ), whereas quinoline complexes show M-N and M-X absorption bands in the far I.R. region. The presence of a single band in the region 580-500 $cm^{-1}$ in all the complexes suggest that the configuration of $SnC_3$ group in $R_3SnX.L$ compounds is planar and that of $R_2SnX_2.L$ is linear.[126]

From the above discussion it has been suggested that in all the complexes of (pyrazolone) antipyrine and 4-amino antipyrine, tin atom is found to be pentacoordinated. A trigonal bipyramidal geometry has therefore been proposed for these complexes. All the complexes of quinoline with $R_3SnX$ and $R_2SnX_2$ are also pentacoordinated except for tributyltin chloride and triphyenyltin chloride complexes of benzo (c) quinoline which have a hexa-coordinated tin atom, having an octahedral geometry. Thus a trigonal bipyramidal geometry for all these compounds containing five coordinate tin atom and an octahedral geometry for TPT and TBT complexes of benzo (c) quinoline having a six coordinate tin atom has been suggested.

# CHAPTER VI

## COMPLEXES OF ORGANOTIN(IV) HALIDES WITH 2,5-DIMERCAPTO-1,3,4-THIADIAZOLE 5,6-DIMETHYL BENZIMIDAZOLE AND 2-BENZIMIDAZOLE THIOL

# COMPLEXES OF ORGANOTIN (IV) HALIDES WITH 2,5-DIMERCAPTO-1,3,4-THIADIAZOLE, 5,6-DIMETHYL-BENZIMIDAZOLE AND 2-BENZIMIDAZOLE THIOL

## EXPERIMENTAL

The organotin (IV) halides (E. Merck), 2,5-dimercapto-1,3,4-thiadiazole m.p. 148°C, 5,6-dimethyl benzimidazole m.p. 204° and 2-benzimidazole thiol m.p. 255-60°C all Koch-Light or A.R. grade were used as received. Solvents used were purified by standard methods.

The I.R. spectra (4000-200 $cm^{-1}$) of the complexes were recorded as nujol mulls on a Perkin Elmer spectrophotometer model 621. The molar conductance measurements were carried on a Systronic conductivity bridge type 302.

### Preparation of the complexes

An equimolar solution of the ligands and the organotin (IV) halides were mixed in stoichiometric ratio. These mixtures were allowed to stand for two or three days when they yielded solid products. They were washed with the solvent and dried in vacuum.

## RESULTS AND DISCUSSION

The analytical results of the complexes (Table 7) support the proposed stoichiometries. Their molar conductances in methanol, nitrobenzene and dimethyl formamide (DMF) has been measured. The values are low, reflecting their covalent nature. The conductivity of the trimethyltin chloride adduct of 2,5-dimercapto-1,3,4-thiadiazole could not be measured due to its insolubility in any suitable solvent. All the complexes were thermally stable and insensitive to oxidation by air.

The coordination behaviour of the ligand has been investigated with the help of infrared spectroscopy. The assignments of various modes of vibrations have been made by analogy with the spectra of similar heterocyclic compounds[177] particularly benzothiazoles.[178] Only significant changes providing information regarding coordination and identification of the donor sites in the complexes have been discussed in detail.

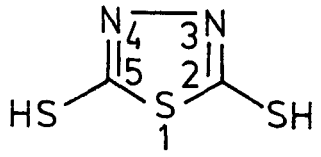
2,5-dimercapto-1,3,4-thiadiazole commonly known as Bismuthiol I has been shown to exist in two isomeric forms, viz., the thione and the mercapto forms. Chemical reactions have revealed that the thione form is predominant with a smaller quantity of mercapto form in equilibrium.[179] The thione form is, therefore, assumed to take part in complexation.

Table 7

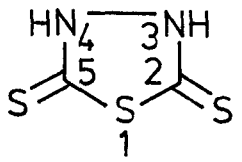
Melting point, analytical data, and Molar Conductance of the Complexes.

| Compounds | M.P. °C | % C Found (calcd.) | % H Found (calcd.) | % N Found (calcd.) | % S Found (calcd.) | % Cl Found (calcd.) | % Sn Found (calcd.) | Molar conductance* $ohm^{-1}$ $cm^2$ $mole^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| TMT (Me.) | 170 | 11.10 (11.07) | 3.36 (3.38) | 8.64 (8.61) | 29.50 (29.52) | 10.90 (10.91) | 36.43 (36.48) | 0.0200 |
| TPT (Me) | 105-10 | 42.22 (42.26) | 3.32 (3.32) | 5.49 (5.47) | 118.75 (18.76) | 6.96 (6.94) | 23.24 (23.20) | 0.0171 |
| DBTA.(Me) | 140 | 46.41 (46.40) | 4.15 (4.18) | 4.55 (4.51) | 15.49 (15.46) | - | 19.12 (19.11) | 0.0182 |
| TMT.(DMB) | 196 | 41.77 (41.72) | 5.54 (5.50) | 8.10 (8.11) | - | 10.25 (10.28) | 34.38 (34.36) | 0.0004 |
| TPT.(DMB) | 185 | 61.02 (61.00) | 4.75 (4.70) | 5.28 (5.27) | - | 6.66 (6.68) | 22.20 (22.21) | 0.0162 |
| DBTA(DMB) | 175 | 50.75 (50.74) | 6.88 (6.84) | 5.60 (5.63) | - | - | 23.85 (23.88) | 0.0171 |
| TMT. (BIT) | 298 | 34.33 (34.37) | 4.26 (4.29) | 8.00 (8.02) | 9.14 (9.16) | 10.18 (10.16) | 33.94 (33.97) | 0.0014 |

* Molar conductance of $10^{-3}$M solutions.



Mercapto



Thiono

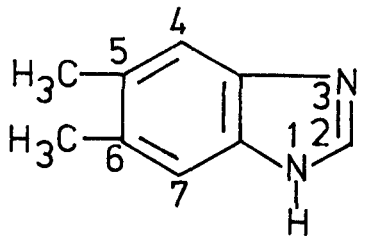
A study of its transition metal complexes has been reported recently from this laboratory.[180-182] Its I.R. spectrum has a weak S-H band at 2690 $cm^{-1}$ suggesting predominance of the thiono form.[183] The N-H stretching frequency in all the complexes is negligibly shifted or almost unchanged. There is no significant change in the C=N stretching frequency of the ligand after the complexation. The $\nu$(C-S) appearing at 715 $cm^{-1}$ in the free ligand has been shifted to a slightly higher wave number in the complexes. However, the strong bands at 1120 and 1055 $cm^{-1}$ in bismuthiol I has been assigned to C=S stretching mode. These bands showed a marked shift in $\nu$ (C=S) upon complexation suggesting the coordination of metal through exocyclic sulphur atom.

The far I.R.spectra of the complexes showed new bands in 400-250 $cm^{-1}$ region. These bands have been assigned to the metal-sulphur and metal-halogen stretching modes. Since there is no band attributable to M-N stretching frequency, it is suggested that the coordination is occurring only through the sulphur atom.

Many transition metal complexes of 5,6-dimethyl benzimidazole and benzimidazole-2-thiol have already been investigated.[178] Since

no work seems to have been done on organotin (IV) halides or acetates it was worth investigating the complexing behaviour of these ligands with organotin (IV) halides.

The main peaks of the I.R. spectra in the region 4000-400 $cm^{-1}$ of the ligands and complexes are mentioned in table 8. The general features of the spectra of the complexes resemble those of the respective free ligand. As these peaks seem to be mainly due to the ligands, their tentative assignments are obtained with reference to those of the benzothiazole or benzimidazole derivatives. In case of 5,6-dimethyl benzimidazole complexes no change in N-H stretching frequency has been observed ruling out the possibility of the coordination of secondary nitrogen atom with tin atom. However, a shift of C-N stretching frequency to lower wave number is indicative of the coordination through tertiary nitrogen atom to the metal. The ring vibrations are



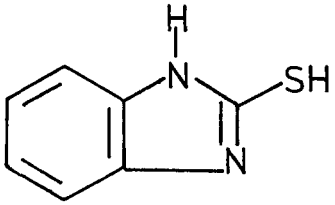

5,6-Dimethyl benzimidazole

observed in the region 700-800 $cm^{-1}$ in all the complexes which do not interfere with the N-H vibration mode. The tin (IV) chloride adduct of benzimidazole-2-thiol also known as 2-mercapto benzimidazole has been reported earlier from this laboratory.[184]

Table 8

IR Spectra of the ligands, complexes and their assignments.

| Compound | ν(S–H) | ν(N–H) | ν(C=N) | ν(C=S) | ν(C–N) | ν(C–S) | ν(M–N) | ν(M–S) |
|---|---|---|---|---|---|---|---|---|
| Bismuthiol | 2490 m | 3060 s<br>2875 s | 1460 s | 1120 s<br>1055 s | 1265 s | 715 s | – | – |
| TMT (Bis). | – | 3125 w<br>2920 s | 1460 s | 1060 w | 1250 w | 720 m | – | 335 w |
| TPT (Bis). | – | 3120 s<br>2920 s | 1465 s<br>1430 w | 1080 w<br>990 s | 1260 w | 725 s | – | 325 m |
| DBTA(Bis) | – | 3135 w<br>2920 w | 1470 s | 1060 s | 1242 w | 720 w | – | 355 m |
| DMB | – | 3050 sh | 1650 w | – | – | – | – | – |
| TMT (DMB) | – | 3050 w | 1620 w | – | – | – | 470 w | – |
| TPT (DMB) | – | 3050 w | 1590 s | – | – | – | – | – |
| DBTA (DMB) | – | 3080 m | 1600 s | – | – | – | 490 w | – |
| BIT | – | 3325 b<br>3150 b | 1615 m<br>1520 s | – | – | – | – | – |
| TMT(BIT) | – | 3160 w<br>3120 w | 1510 s<br>1470 s | – | – | – | 598 m | – |




Benzimidazole-2-thiol

It has been established earlier that the benzimidazole molecule coordinates through the pyridyl nitrogen.[184,185] This has also been supported by I.R. studies.[185-188] A strong band at 1520 $cm^{-1}$ and another band of medium intensity at 1615 $cm^{-1}$ appeared in the I.R. spectrum of the free ligand which are attributed to the C=N stretching mode. These bands showed a marked negative shift in the spectrum of trimethyl tin chloride adduct of benzimidazole 2-thiol. Further, the S-H and N-H frequencies are almost unchanged in the complexed ligand. It suggests that only the pyridyl nitrogen of benzimidazole ring coordinates to tin atom being a more basic site than the imino nitrogen and the sulphur atom of the thiol group.

The absorption bands in the far I.R. region of the complexes are not well resolved and hence tentative assignments have been made. These peaks are attributed to the metal-nitrogen and metal halogen frequencies (table 8).

The tin atom in all the complexes described above is found to be pentacoordinated hence a trigonal bipyramidal geometry has been proposed for all these complexes.

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